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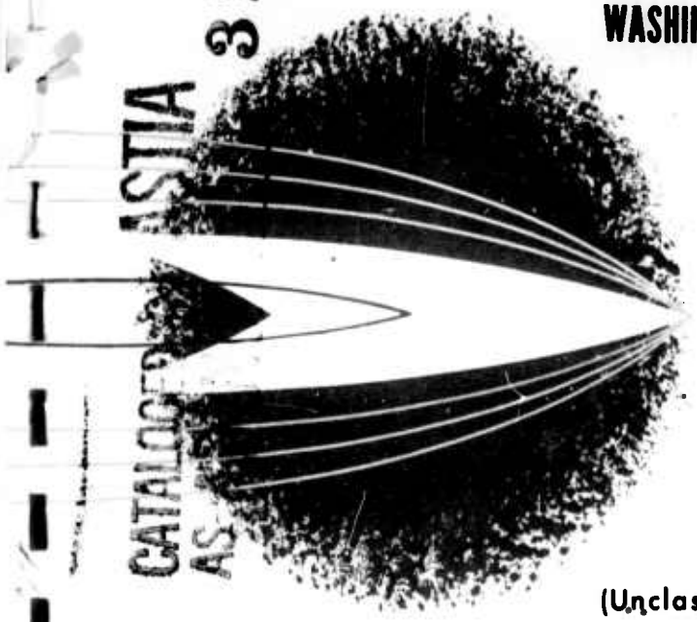

14 July 1961
Report No. 0235-01-11
(Quarterly)
Copy No. AF-12-1

(Unclassified Title)

RESEARCH IN FLUORO-NITRO COMPOUNDS

Contract Nonr-2655(00)
ARPA Order No. 170-61, Project Code 9100

★

Chemical Division

Aerojet-General CORPORATION

AZUSA, CALIFORNIA — THE GENERAL TIRE — SACRAMENTO, CALIFORNIA

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

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7 August 1961

TO: U.S. Navy
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Washington, D.C.

SUBJECT: Report No. 0235-01-11
Research in Fluoro-Nitro Compounds
(Unclassified Title)

CONTRACT: Nonr 2655(00)
ARPA Order No. 170-61, Project Code 9100

ERRATA

Figure 3a should be added to the report. Figures 4, 10, and 11 should be replaced by the new sheets enclosed.

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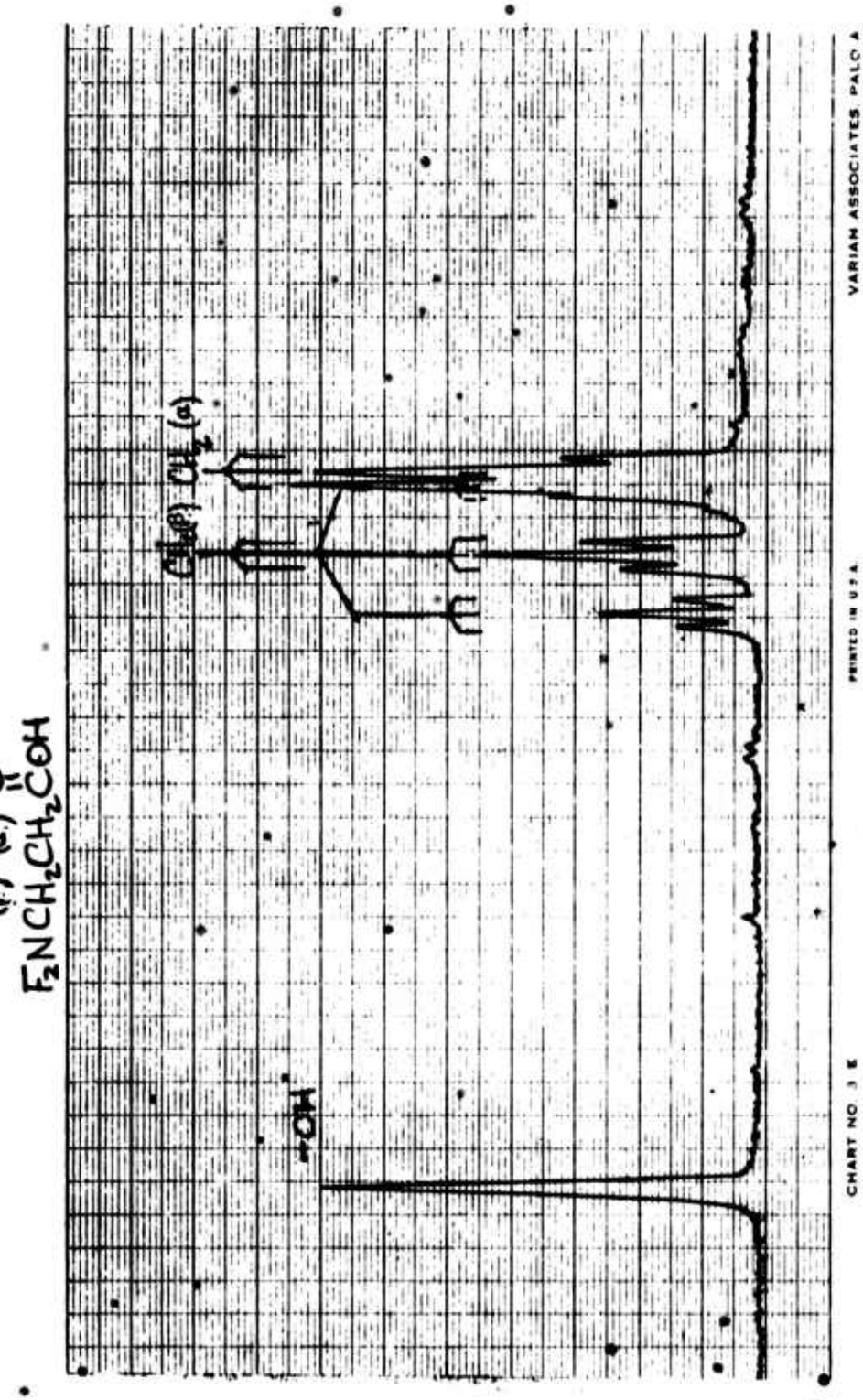
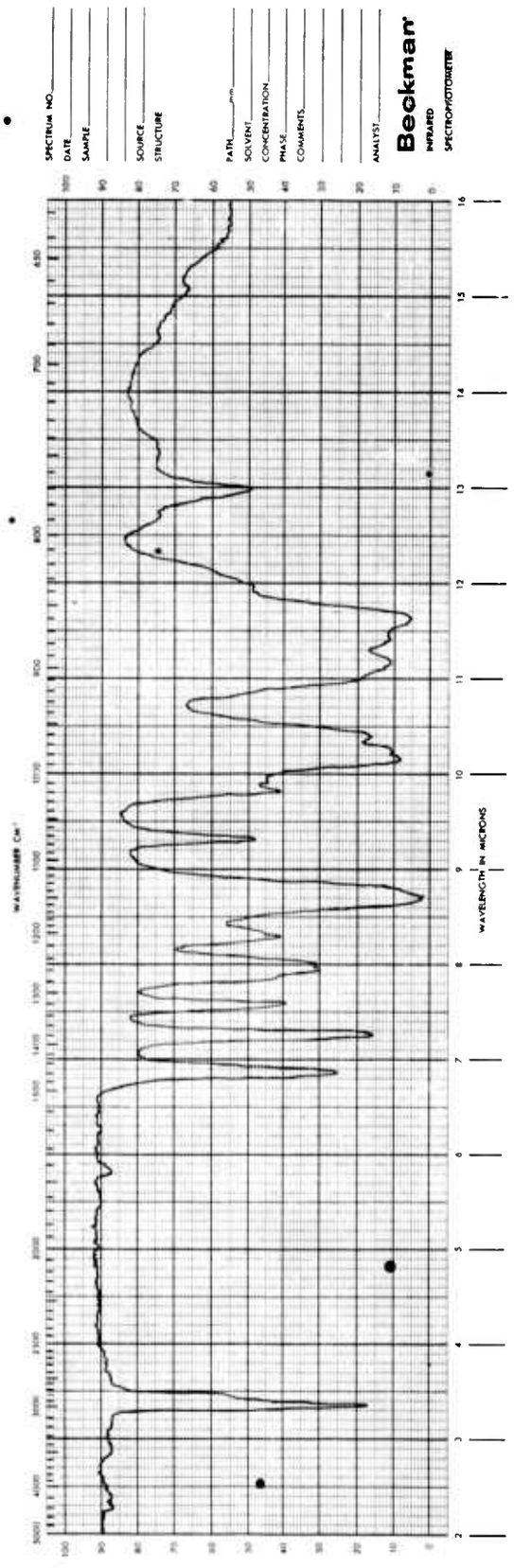


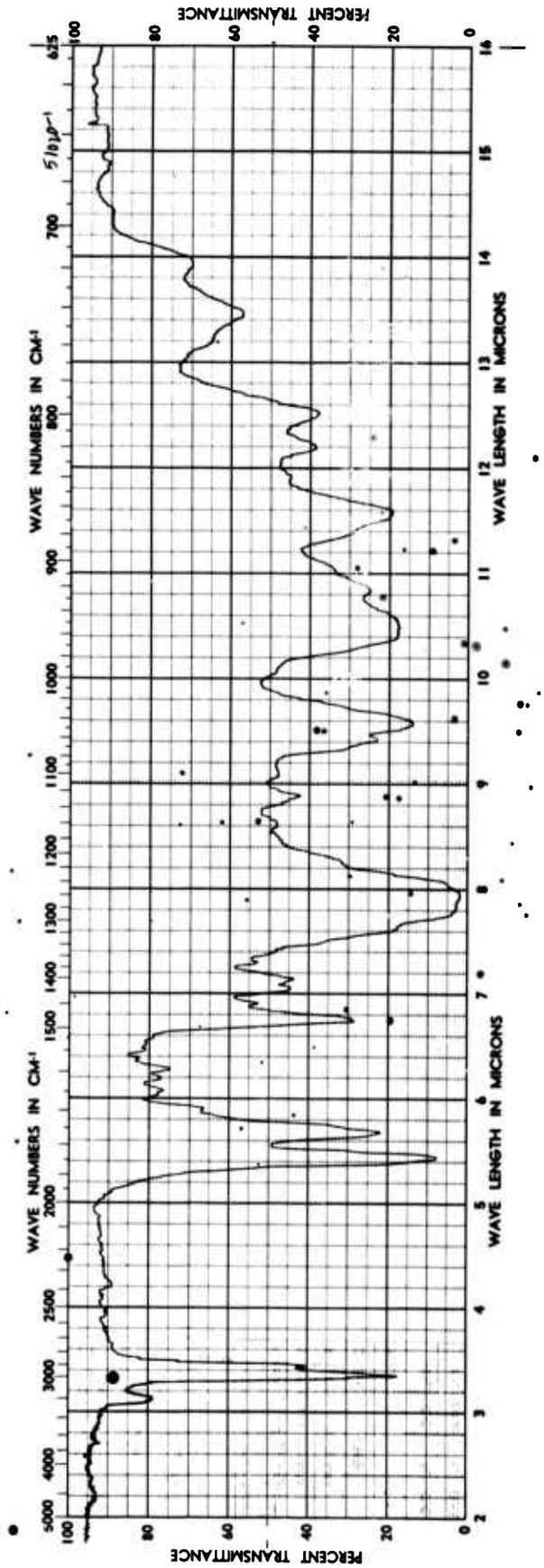
Proton NMR Spectrum of β-Difluoraminopropionic Acid

Figure 3a



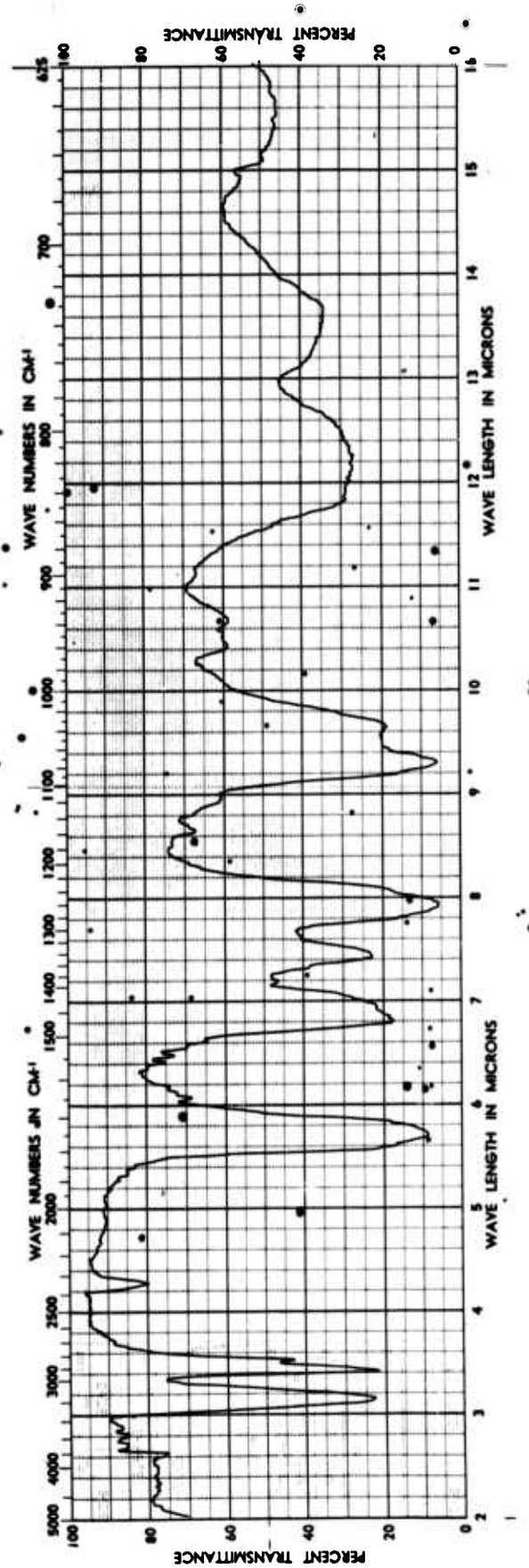
2,5,5-Trimethyl-2-(difluoramino)tetrahydrofuran

Figure 4



n-Butyl N,N-Difluorocarbamate

Figure 10



n-Buyl N-Fluorocarbamate

Figure 11

14 July 1961

Report No. 0235-01-11
(Quarterly)

RESEARCH IN FLUORO-NITRO COMPOUNDS

Contract Nonr 2655(00)
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ABSTRACT

Difluoramine (in sulfuric acid) was added to the double bonds of acrylic acid and methyl vinyl ketone. The latter adduct was converted to tris(difluoramino)butane. Cyclic NF compounds were formed from 5-hexene-2-one and 5-methyl-5-nitro-2-hexanone. Acetylene underwent the addition of two moles of difluoramine. In the case of propargyl chloride, the product was identical to that prepared from chloroacetone.

Ethyl N-fluorocarbamate formed a stable anion, which was converted to the N-methyl, N-chloro, and N-bromo derivatives. N-Fluorimino dicarboxylic acid diethyl ester was formed by the reaction of this anion with ethyl chloroformate, N-bromo-N-fluorocarbamate, or dichlorofluoramine. Dichlorofluoramine was formed from the reaction of sodium hypochlorite with ethyl N-fluorocarbamate, ethyl N-chloro-N-fluorocarbamate, or N-fluoriminodicarboxylate. Butyl N,N-difluorocarbamate was prepared by a fluorination in ethylene dichloride.

Side products in the aqueous fluorination of urea were identified as biurea and azodicarbodiamide.

An unstable product was obtained from the reaction of tetrafluorohydrazine with dichlorofluoramine.

CONTENTS

I. INTRODUCTION

The objective of this work is to develop new methods of preparing high-energy materials which are of interest for military applications.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINES (K. Baum)

1: Discussion

The reactions of several ketones with difluoramine in sulfuric acid have produced gem-difluoramines, although cyclic difluoraminoethers or lactones were formed from some ketones with oxygen-containing functional groups.* This investigation was continued, with emphasis on determining the effects of functional groups and unsaturation on the reaction.

Tertiary alkyl difluoramines have been prepared previously by the reaction of difluoramine in sulfuric acid with olefins capable of forming tertiary carbonium ions, although the analogous compounds were not formed from olefins capable of forming secondary carbonium ions.** It might therefore be possible to selectively react the carbonyl of an unsaturated ketone to form a gem-difluoramino olefin.

When 5-hexene-2-one was used as the starting material, this course was not followed. The product was soluble in concentrated sulfuric acid, and was isolated by quenching the acid with ice. The elemental analysis indicated the structure 2,5-dimethyl-2-(difluoramino)tetrahydrofuran. The infrared spectrum (Figure 1) was similar to that of 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran.*** The reaction apparently proceeds by protonation of the

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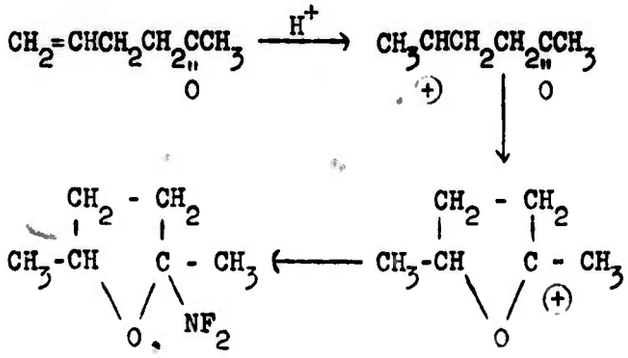
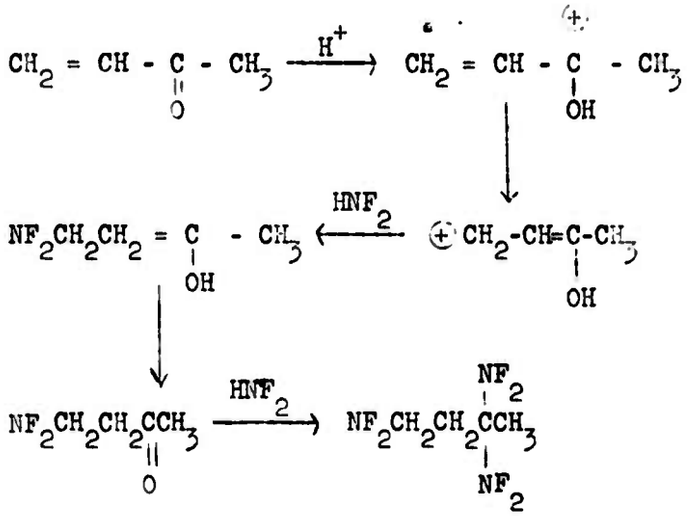
**Aerojet-General Report No. 0235-01-10, 14 April 1961 (Confidential). Rohm and Haas Co., Quarterly Report on Synthetic Chemistry, Part II, 18 November 1960, p. 23 (Confidential).

***Aerojet-General Report No. 0235-01-10, 14 April 1961, Fig. 7 (Confidential).

olefin, followed by cyclization and attack on difluoramine:



The reaction of methyl vinyl ketone with difluoramine in sulfuric acid has yielded tris(difluoramino)butane. The infrared spectrum of this product is shown in Figure 2. When an insufficient amount of difluoramine was used, however, a product was formed which retained the infrared carbonyl band of the starting material, but lost the olefin band. Thus, the first step appears to be an acid-catalyzed Michael addition followed by the replacement of the carbonyl.



The initially formed carbonium ion would react with difluoramine to give predominately the terminally substituted product, since addition to the carbon containing the hydroxyl group should be rapidly reversible.

This mode of addition was confirmed for the acid-catalyzed addition of difluoramine to acrylic acid to give β-(difluoramino)propionic acid. The infrared and proton NMR spectra* are shown in Figure 3. The F^{19} NMR spectrum gave the expected triplet due to coupling with the adjacent CH_2 group broadened by N^{14} quadruple interaction.

$$CH_2 = CHCOOH \xrightarrow{H^+} CH_2 = CH - \overset{(+)}{C}(OH) - OH \longleftrightarrow (+)\,CH_2 - CH = C(OH) - OH$$

$$NF_2CH_2CH_2COOH \xleftarrow{HNF_2} (+)\,CH_2 - CH = C(OH) - OH$$

Previous attempts to prepare gem-difluoramines from polynitroketones were unsuccessful.** The investigation has now been extended to mononitroketones. 5-Methyl-5-nitro-2-hexanone*** underwent a novel denitration reaction to give 2,5,5-trimethyl-2-(difluoramino)tetrahydrofuran. This product was identified by analysis and by its infrared spectrum (Figure 4) which is similar to those of the other α-(difluoramino)tetrahydrofurans which were prepared in this study. This reaction probably took place by the protonation of the nitro group followed by the loss of nitrous acid, possibly with assistance by the carbonyl:

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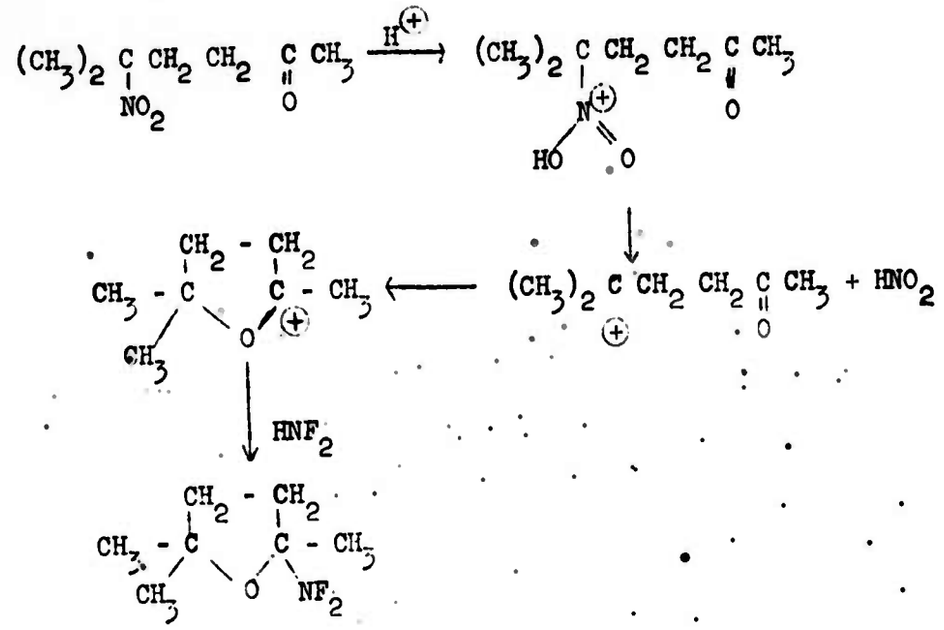
*We are indebted to Dr. D. W. Moore, U.S. Naval Ordnance Test Station, China Lake, California, for the NMR analysis.

**Aerojet-General Report No. 0235-01-10, 14 April 1961 (Confidential).

***H. Schechter, J. Am. Chem. Soc., 74, 3664 (1952).



When 5-nitro-2-hexanone* was used as the starting material, this reaction was not observed. The infrared spectrum of the product showed NF_2 and nitro bands, but only a trace of carbonyl. The boiling point (54°/0.1 mm) was close to that of the starting material (65°/0.08 mm), as has been found to be the case for most gem-difluoramines derived from ketones. The product of the preceding reaction, on the other hand, distilled at 50°/19 mm. Vapor-phase chromatography indicated that the sample contained 25% of the starting material. An attempt to obtain an analytical sample by this method gave an unstable material. This work will be repeated in order to determine whether the product is the desired gem-difluoramino nitro compound.

The reaction of propionaldehyde with difluoramine in sulfuric acid previously gave a mixture of α, α'-bis(difluramino)propyl ether and 1,1-bis(difluoramino)propane.**

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*Ibid.

**Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 9 (Confidential).

$$CH_3CH_2CHO \xrightarrow[H_2SO_4]{HNF_2} CH_3CH_2\underset{\displaystyle NF_2}{\overset{\displaystyle NF_2}{\underset{|}{\overset{|}{CH}}}} + CH_3CH_2\underset{\displaystyle NF_2}{\overset{\displaystyle NF_2}{\underset{|}{\overset{|}{CH}}}}\text{-}OCHCH_2CH_3$$

The relative amounts of these products depended on the amount of sulfuric acid used. This reaction has been repeated, using fuming sulfuric acid instead of the 96% reagent, and the product consisted almost entirely of the gem-difluoramine.

The reactions of paraformaldehyde or trioxane with HNF_2 in sulfuric acid have given α, α'-bis(difluoramino)methyl ether rather than bis-(difluoramino)methane.* However, the importance of the acid in determining the course of the reaction with propionaldehyde suggested that fuming sulfuric acid would be a more satisfactory reagent than concentrated acid for preparing bis(difluoramino)methane. A scouting experiment on this reaction did not produce the difluoraminoether. A gaseous product was formed with strong infrared peaks at 10.0 and 10.4 μ, peaks which are usually found in gem-difluoramines. This product has not yet been isolated in pure form.

The reaction of chloral hydrate with difluoramine in concentrated sulfuric acid did not give a product insoluble in the acid. The infrared spectrum of the material that was isolated after water-quenching suggested a mixture of the starting material and the alcohol derived from the addition of difluoramine to the carbonyl.

A new reaction for the synthesis of NF compounds is the acid-catalyzed addition of difluoramine to acetylenes. This reaction was carried out in the same manner as the reaction of difluoramine with carbonyl compounds in sulfuric acid. Both 1-hexyne and 3-hexyne gave bis(difluoramino)hexanes, as shown by elemental analysis. The direction of these additions is not known, inasmuch as the results of NMR analyses are not yet available.

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*Quarterly Progress Report on Synthetic Chemistry, Rohm and Haas Co., Report No. P-60-24, Pt. II, 13 February 1961, p. 5 (Confidential); Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 9 (Confidential).

In order to test the possibility that the addition of HNF_2 to acetylenes proceeds through the hydration of the triple bond to give a ketone a control experiment was carried out. 3-Hexyne was treated with sulfuric acid under approximately the conditions used for the HNF_2 reactions. A 50% yield of 3-hexanone was isolated. Although this result suggests that the HNF_2 addition follows the hydration of the triple bond, the possibility that the direct addition of HNF_2 to the triple bond takes place at a faster rate than hydration cannot be ruled out.

The addition of HNF_2 to propargyl chloride has also been accomplished. The product was 1-chloro-2,2-bis(difluoramino)propane which was identical with the product previously obtained from chloroacetone.*

$$HC \equiv C\,CH_2\,Cl \xrightarrow[H_2SO_4]{HNF_2} CH_3\,\overset{\displaystyle NF_2}{\underset{\displaystyle NF_2}{\overset{|}{\underset{|}{C}}}}\,CH_2\,Cl$$

1,6-Heptadiyne gave a complex high-boiling product which showed infrared absorption due to NF, as well as carbonyl and hydroxyl groups. Phenylacetylene gave a vigorous evolution of gas when it was added to difluoramine and sulfuric acid. No product was isolated.

The reaction of furans with difluoramine in sulfuric acid was also undertaken as an extension to the addition of difluoramine to unsaturated compounds. 2,5-Dimethylfuran yielded a material with a very simple infrared spectrum (Figure 5). The relatively weak absorption in the range from 7.5 to 9.5μ suggests the absence of an ether linkage. However, the analytical results that have been obtained cannot be rationalized. Two attempts to use furan as the starting material resulted in explosions after the addition of the first drop to the mixture of difluoramine and sulfuric acid.

The acid-catalyzed reactions of several ketoacids have been carried out, although analytical data was not obtained because the products

*Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 12 (Confidential).

presented difficult problems in purification. However, the infrared spectra indicated that N-F-containing acids were formed from pyruvic acid, 2-ketoglutaric acid, and 5-ketohexanoic acid.

The preparation of the gem-difluoramine from propionaldehyde using fuming sulfuric acid as the solvent suggested that the cyclic ethers and lactones formed in other reactions using concentrated acid might also be converted to the gem-difluoramines with the fuming acid. The reaction of levulinic acid, which previously gave 4-(difluoramino)-γ-valerolactone,* was therefore repeated using fuming sulfuric acid. A 75% yield of the lactone was obtained.

2. Experimental

a. 2,5-Dimethyl-2-(Difluoramino)tetrahydrofuran

The general procedure used for the difluoramine reactions was described previously.**

Approximately 7 g of difluoramine was generated and allowed to reflux over 2.45 g (0.025 mole) of 5-hexene-2-one. After refluxing began, reaction exotherm raised the temperature from 4 to 30°C. After the temperature again dropped to 0°F, 15 ml of concentrated sulfuric acid was added dropwise. After 4.5 hr the difluoramine was removed and the homogeneous acid solution was poured over 150 ml of cracked ice. A heavy oil separated, and the aqueous mixture was extracted with four 50-ml portions of methylene chloride and the methylene solution was dried over sodium sulfate and distilled. The residue, 3 g, was vacuum-distilled to yield 2.6 g (0.0172 mole, 69% yield) of 2,5-dimethyl-2-(difluoramino)tetrahydrofuran, bp 34°C/8 mm; n_D^{25} 1.3970.

Anal. calc'd for $C_6H_{11}NF_2O$:

C, 47.7; H, 7.29; N, 9.28

Found: C, 47.6; H, 7.17; N, 9.61.

*Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 6 (Confidential).

**Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 10 (Confidential).

b. β-(Difluoramino)propionic Acid

To a refluxing mixture of 8 g of difluoramine and 15 ml of concentrated sulfuric acid was added dropwise 40 g (0.0546 mole) of acrylic acid stabilized with methylene blue. After 2 hr, the solution was poured over ice, and the product was extracted with methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled to yield 4.6 g (67% yield) of β-(difluramine)propionic acid, bp 57-60°C/1 mm; n_D^{25} 1.3899.

Anal. calc'd for $C_3H_5NF_2O$:

C, 28.8; H, 4.0; N, 11.2

Found: C, 25.8; H, 4.28; N, 11.2.

c. Tris(difluoramino)propane

To a refluxing mixture of 6 g of difluoramine and 20 ml of sulfuric acid was added dropwise 2.0 g (0.28 mole) of methyl vinyl ketone. The ketone dissolved initially, and after 2 hr an orange layer began to separate. After another 2 hr, the excess difluoramine was removed, and the product was vacuum-transferred into a -80°C trap at 1 mm Hg. Distillation then gave 0.6 g of tris(difluoramino)propane, bp 58°C/38 mm. An analytical sample was prepared by vapor-phase chromatography.

Anal. calc'd for $C_4H_7N_3F_6$

C, 22.74; H, 3.31; N, 19.90

Found: C, 23.1; H, 3:51; N, 19.90.

d. 2,5,5-Trimethyl-2-(difluoramino)tetrahydrofuran

To a refluxing solution of 4.5 ml (0.03 mole) of 5-nitro-5-methyl-2-hexanone and 8 g of difluoramine was added dropwise 15 ml of concentrated sulfuric acid. The temperature of the solution was maintained between -30 and -20°C by partial immersion of the stirred reactor in a -80°C bath.

Refluxing was then continued without external cooling for 3 hr. The reactor was then cooled to 0° while the excess difluoramine was swept out by a nitrogen stream. The solution was poured over 200 ml of ice. A colorless liquid separated, and the mixture was extracted with four 50-cc portions of methylene chloride. The extracts were combined, washed with distilled water, and dried 80 hr over Drierite. The solution was filtered and the solvent distilled off, yielding a reddish-brown liquid which was vacuum-distilled at 50-51.5°C/18.5-19 mm to yield 3.3 g of colorless liquid. Vapor-phase chromatography indicated that the sample consisted of two components in the ratio 9:1. The major component was separated and submitted for elemental analysis.

Anal. calc'd for $C_7H_{15}NF_2O$:

C, 50.9; H, 7.98; N, 8.48

Found: C, 50.8; H, 7.85; N, 8.57.

e. Reaction of 3-Hexyne with Difluoramine

To a refluxing mixture of 7 g of difluoramine and 15 ml of concentrated sulfuric acid, 2.05 g (0.025 mole) of 3-hexyne was added dropwise. The reaction was highly exothermic, and external cooling was necessary during the addition, in order to keep the temperature at -15 to -20°C. An upper layer separated from the sulfuric acid. After 4 hr, the excess difluoramine was removed, and the product was vacuum-transferred into a -80°C trap at 1 mm Hg. The product consisted of 1.3 g of colorless liquid. The vapor-phase chromatograph indicated that the sample consisted of 94% adduct and 6% 3-hexyne; an analytical sample was prepared with this tool.

Anal. calc'd for $C_6H_{12}N_2F_4$:

C, 38.26; H, 6.44; N, 14.88

Found: C, 37.6; H, 6.30; N, 14.76.

f. Reaction of 3-Hexyne with Sulfuric Acid

3-Hexyne (1.0 g, 0.0122 mole) was added dropwise with stirring to 15 ml of concentrated sulfuric acid at -8°C. Solution occurred slowly with darkening. The acid solution was allowed to stand at ambient temperature for 2 hr and then was poured over 150 ml of ice. The ice was allowed to melt, and the resulting mixture was extracted with four 50-ml portions of methylene chloride. The combined methylene chloride layers were washed with 50 ml of water and dried over sodium sulfate, and the solvent was distilled off. Distillation of the residue gave 0.6 g (0.006 mole, 49% yield) of 3-hexanone, bp 124°, n_D^{25} 1.3994.

g. Reaction of 1-Hexyne with Difluoramine

1-Hexyne (1.08 g, 0.013 mole) was added dropwise to 8 ml of concentrated sulfuric acid and 7 g of difluoramine at reflux. After 2.5 hr, the excess difluoramine was removed, and the product, which formed a separate layer over the sulfuric acid, was vacuum-transferred into a -80°C trap at 1.5 mm Hg. The product, 0.8 g, was shown to be a single compound by vapor-phase chromatography:

Anal. calc'd for $C_6H_{12}N_2F_4$:

C, 38.26; H, 6.44; N, 14.88

Found: C, 38.20; H, 6.44; N, 14.43.

h. 1-Chloro-2,2-bis(difluoramino)propane

To a refluxing mixture of 8 g of difluoramine and 15 ml. of concentrated sulfuric acid, 1.87 g (0.025 mole) of propargyl chloride was added dropwise. After 3 hr of reflux, the excess difluoramine was removed and the product was transferred at 90 mm into a -80°C trap to give 0.2 ml of a colorless liquid after difluoramine was removed by flushing with nitrogen. The infrared spectrum was identical to that of 1-chloro-2,2-bis(difluoramino)propane which was prepared from chloroacetone.*

*Aerojet-General Report No. 0235-01-10, 14 April 1961, Figure 5 (Confidential).

i. Reaction of 2,5-Dimethylfuran with Difluoramine

To a refluxing mixture of 8 g of difluoramine and 15 ml of concentrated sulfuric acid was added dropwise 2.4 g (0.025 mole) of 2,5-dimethylfuran. The reaction was highly exothermic, requiring carefully controlled addition. A separate dark-red layer was present immediately after the addition, but dissolved slowly. A low-boiling red liquid refluxed with the difluoramine but was slowly swept out by the nitrogen stream. After 2 hr the excess difluoramine was removed and a separate layer which had again formed was vacuum-transferred at 1 mm Hg into a -80°C trap.

Anal., found: C, 32.9, 32.6; H, 6.01; 6.27;
N, 15.69; 15.57.

B. PREPARATION AND REACTIONS OF N-FLUOROCARBAMATES (V. Grakauskas)

1. Discussion

Ethyl N-fluorocarbamate has been prepared by the fluorination of aqueous ethyl carbamate.* A study of the properties of this interesting compound is now being made.

The NMR spectrum** of this compound is consistent with the assigned structure. It is interesting that the NF resonance is high field from trifluoroacetic acid. The position of the NH compares with that in nitramines. It was found that ethyl N-fluorocarbamate could be dissolved in aqueous alkali at 0-10°C without decomposition and could be recovered on acidification. This is the first example of a stable NF anion. The infrared and NMR spectra are shown in Figures 6 and 6a.

$$C_2H_5OCNHF \xrightarrow{OH^-} C_2H_5OCNF^{\ominus}$$
(O)

*Aerojet-General Corp. Report No. 0371-02-3 (Quarterly), High-Energy Oxidizer Binders for Solid Propellants, 14 October 1960 (Confidential).

**We are indebted to Dr. J. P. Freeman, Rohm and Haas Co., for the NMR analysis.

The sodium salt of ethyl N-flourocarbamate reacted readily at 5-10°C with dimethyl sulfate, and the product of this reaction was identified as ethyl N-fluoro-N-methylcarbamate. This compound was also prepared in low yield by direct fluorination of aqueous ethyl N-methylcarbamate:

$$\ominus\ NFCO_2C_2H_5 \xrightarrow{(CH_3)_2SO_4} CH_3NFCO_2C_2H_5$$

$$CH_3NHCOOC_2H_5 + F_2 \xrightarrow{(H_2O)} CH_3NFCOOC_2H_5$$

The sodium salt of ethyl N-fluorocarbamate reacted with chlorine and bromine to give the corresponding N-chloro and N-bromo derivatives. Both compounds were obtained in good yields and their structures were confirmed by elemental analysis. It is interesting to note that, except for very slight difference in the 12-13μ range, the infrared spectra of ethyl N-chloro-N-fluoro- and ethyl N-bromo-N-fluorocarbamate are identical (Figures 7 and 8).

The sodium salt of ethyl N-fluorocarbamate also reacted with ethyl chloroformate in aqueous solution to give N-fluorimino dicarboxylic acid diethyl ester in good yields:

$$Na^{\oplus}\ \overset{\ominus}{N}FCOOC_2H_5 + ClCOOC_2H_5 \xrightarrow{(H_2O)} NF(COOC_2H_5)_2$$

The product, a high-boiling yellow oil, was isolated and identified on the basis of its infrared spectrum (Figure 9) and elemental analyses. N-Fluorimino dicarboxylic acid diethyl ester was also obtained as a side product in the halogenation of the sodium salt of ethyl N-fluorocarbamate.

Attempts to synthesize N,N'-difluorohydrazodicarboxylate by reacting the sodium salt of ethyl N-fluorocarbamate with ethyl N-bromo-N-fluorocarbamate led to the formation of N-fluoriminodicarboxylate:

$$Na^{\oplus}\ \overset{\ominus}{N}FCOOC_2H_5 + BrNFCOOC_2H_5 \longrightarrow NF(COOC_2H_5)_2$$

Similarly, the N-fluoriminodicarboxylate was produced in the reaction between dichlorofluoramine and the sodium salt of ethyl N-fluorocarbamate:

$$Cl_2NF + 2\ Na^{\oplus}\overset{\ominus}{N}FCOOC_2H_5 \longrightarrow NF(COOC_2H_5)_2$$

In this latter case the objective was to synthesize perfluorotriazenedicarboxylate, $NF(NFCOOC_2H_5)_2$.

Results of the latter two experiments seem to suggest that both N,N'-difluorohydrazo- and perfluorotriazenedicarboxylate are unstable reaction intermediates and undergo decomposition in an aqueous medium with the formation of N-fluoriminodicarboxylate. Considerable amounts of carbon dioxide and nitrous oxide (N_2O) were produced in these reactions.

Attempts to nitrate ethyl N-fluorocarbamate with ethyl nitrate in concentrated sulfuric acid, with the objective of synthesizing ethyl N-fluoro-N-nitrocarbamate, failed to give the desired product. Instead, a vigorous evolution of gaseous products took place, which were identified as carbon dioxide and nitrous oxide:

$$NHFCOOC_2H_5 + C_2H_5ONO_2 \xrightarrow{H_2SO_4} N_2O + CO_2$$

Although aqueous sodium N-fluorocarbamate was relatively stable at low temperatures, it underwent spontaneous decomposition when it was allowed to warm up to 20-25°C. The decomposition was highly exothermic, and a water-insoluble colorless liquid separated from the reaction mixture during the course of the reaction. This material has not yet been identified, but its infrared spectrum suggests that the compound is a carbamate. However, it is not one of the expected decomposition products: hydrazodicarboxylate, azodicarboxylate, iminodicarboxylate, or diethyl oxalate.

In addition to the high-boiling liquid, small amounts of gaseous materials were produced during the decomposition of aqueous sodium N-fluorocarbamate. These were identified by infrared spectrum as a mixture of carbon dioxide and ethylene. The latter is apparently produced from the ethyl group of the carbamate. Still another product of this reaction, sodium fluoride, was isolated and identified.

The first step of the decomposition of the sodium salt of ethyl N-fluoro-carbamate may involve the elimination of fluoride anion with the formation of a biradical:

$$Na^{\oplus}\ {}^{\ominus}NFCOOC_2H_5 \xrightarrow[\Delta]{H_2O} :NCOOC_2H_5 + NaF$$

The expected dimerization product of the biradical, azodicarboxylic acid ester was not found.

Several preliminary attempts have been made to explore the uses of ethyl N-fluorocarbamate and N-fluoriminodicarboxylate as fluorinating agents. In one experiment, ethyl N-fluorocarbamate was reacted with naphthalene in concentrated sulfuric acid, with the objective of synthesizing 1-fluoro-naphthalene. This reaction would parallel the bromination of naphthalene with N-bromosuccinimide. No reaction was observed at 0-20°C. When the mixture was warmed to 50-55°C, the solid naphthalene gradually disappeared. However, when the reaction mixture was poured on ice, a clear solution resulted, suggesting that naphthalene was sulfonated rather than fluorinated. Furthermore, the aqueous solution possessed strong oxidizing properties, and ethyl N-fluoro-carbamate was recovered on extraction with methylene chloride.

Another attempt has been made to use N-fluorocarbamate for NF fluorination. A mixture of ethyl N-fluorocarbamate and acetamide was heated to 90-95°C and kept at this temperature for a period of several hours. The expected N,N-difluoroacetamide was not obtained in this reaction, and at the end of the run large amounts of unreacted N-fluorocarbamate were isolated.

One unsuccessful attempt was also made to use N-fluoriminodicarboxylate as a fluorinating agent. An equimolar mixture of the material and naphthalene was kept at 90-95°C for 7 hr without any apparent reaction.

Both N-chloro-N-fluoro- and N-bromo-N-fluorocarbamates are useful as intermediates for the preparation of NF compounds. Thus, ethyl N-chloro-N-fluorocarbamate reacted instantaneously with sodium hypochlorite to give dichlorofluoramine:

$$ClNFCOOC_2H_5 + NaOCl \longrightarrow Cl_2NF + CO_2$$

Dichlorofluoramine has been previously synthesized by the Allied Chemical Corporation* by reacting sodium azide with chlorine fluoride (ClF). The physical properties and infrared spectrum of the Aerojet-General product agree with those reported by Allied Chemical. Dichlorofluoramine was also obtained by reacting ethyl N-fluorocarbamate with sodium hypochlorite:

$$HNFCOOC_2H_5 + NaOCl \longrightarrow Cl_2NF + CO_2$$

N-Fluoriminodicarboxylate also reacted with aqueous sodium hypochlorite to give dichlorofluoramine:

$$NF(COOC_2H_5)_2 + NaOCl \longrightarrow Cl_2NF + CO_2$$

Similar reactions might be used to prepare other nitrogen halides.

Attempts to prepare N-chloro-N-fluoroethyl amine by the reactions of ethyl N-fluoro-N-methylcarbamate with aqueous sodium hypochlorite, at 0-5°C or at 35°C, were unsuccessful. The starting material was recovered.

$$RNFCOOR' + NaOCl \not\longrightarrow RNFCl + CO_2 + R'OH$$

*Allied Chemical Corporation, General Chemical Division, Quarterly Progress Report, April-June 1960, Contract No. DA-30-069-ORD-2638 (Confidential).

Since the fluorination of aqueous carbamates gave a mixture of the monofluoro derivative and difluoramine, it appears the difluorocarbamates are hydrolytically unstable. The fluorination of n-butylcarbamate was therefore carried out in ethylene dichloride to prepare N,N-difluorocarbamate in ca. 40% yield. The infrared spectrum (Figure 10) and elemental analysis confirmed the structure. The infrared spectrum of n-butyl N-fluorocarbamate is shown in Figure 11. An attempt to prepare ethyl N,N-difluorocarbamate by this method resulted in difficulties because the product apparently boils at about the same temperature as the solvent.

The expected hydrolytic instability of butyl N,N-difluorocarbamate was confirmed in a reaction with water at 30-50°C to yield difluoramine and carbon dioxide:

$$NF_2COOC_4H_9 + H_2O \longrightarrow HNF_2 + CO_2 + C_4H_9OH$$

Alkyl N,N-difluorocarbamates might therefore be used as intermediates for the production of difluoramine. Carbon dioxide-free difluoramine could possibly be obtained by reacting N,N-difluorocarbamates with alcohols.

n-butyl N,N-difluororcarbamate was found to react readily with aqueous sodium hypochlorite to give chlorodifluoramine:

$$NF_2COOC_4H_9 + NaOCl \longrightarrow ClNF_2 + C_4H_9OCOONa .$$

The infrared spectrum indicated a high-purity product, not contaminated by carbon dioxide or tetrafluorohydrazine. This reaction offers a simple route to chlorodifluoramine.

2. Experimental

a. Preparation of Ethyl N-Fluorocarbamate

A solution of 270 g ethyl carbamate (3.0 moles) in 3000 ml H_2O was fluorinated at 0-5°C with elementary fluorine (diluted with nitrogen, 1:4) until ca. 80 liters of fluorine gas was absorbed (7.0 hr). The

clear and colorless aqueous solution was extracted with 15 250-ml portions of methylene chloride and the combined extracts were dried over Drierite. The solution was filtered and the clear filtrate was concentrated at 20-30°C and 20-25 mm Hg pressure to remove the solvent. The residue, a pale-yellow liquid, was fractionated at reduced pressure to give 75 g of colorless liquid, bp 30°C/0.1-0.3 mm, n_D^{25} 1.3950. This material was identified as pure ethyl N-fluorocarbamate by comparing its infrared spectrum and refractive index with those of a known sample.

The distillation residue, amounting to 150 g, consisted of a mixture of ethyl carbamate and ethyl N-fluorocarbamate. Attempts to remove the latter by further distillation gave liquid fractions of higher refractive index than that of ethyl N-fluorocarbamate. No attempts have been made to determine how much of the product remained in the residue.

A sample of the residue was dissolved at 0-5°C in excess aqueous 20% sodium hydroxide and the solution was extracted several times with methylene chloride solution. The alkaline aqueous solution was acidified with hydrochloric acid at 0-5°C and the mixture extracted with methylene chloride. Pure ethyl N-fluorocarbamate was isolated from this solution.

b. Fluorination of Ethyl Carbamate in Ethylene Chloride Solution

A solution of 8.9 g ethyl carbamate (0.1 mole) in 350 ml ethylene chloride was fluorinated with elementary fluorine diluted with nitrogen (1:5) at -20 to -25°C until 4.5 liters of fluorine gas was passed into the reaction mixture. The solution remained clear and colorless throughout the run and the fluorine was consumed. On distillation of the reaction mixture, it was found that the product co-distills with the solvent. The infrared spectrum of the solution indicated that the expected product was produced. No further attempts have been made to isolate the product.

c. Fluorination of n-Butylcarbamate in Ethylene Chloride Solution

A solution of 9.4 g n-butylcarbamate (0.08 mole) in 350 ml dry ethylene chloride was fluorinated with elementary fluorine diluted with nitrogen (1:5) at -10°C until 3.5-4.0 liters of fluorine gas was passed into the reaction mixture. At the end of the run, the clear, colorless solution was concentrated to remove the solvent and the pale yellow residue was distilled at reduced pressure to yield 6 g of colorless liquid, bp 60-65°C/20-25 mm, n_D^{25} 1.3780. The material was redistilled and a middle cut, n_D^{25} 1.3710, was submitted for infrared and elementary analyses. The infrared spectrum showed strong carbonyl absorption, several peaks in the NF region (10-12 μ), and absence of NH absorption at 2.8-3.2 μ.

Calculated for $C_5H_9F_2NO_2$:

C, 39.22; H, 5.92; F, 24.82; N, 9.14

Found: C, 39.70; H, 6.45; F, 21.40; N, 9.16.

d. Preparation of n-Butyl N-fluorocarbamate

A solution (partially in suspension) of 12 g n-butyl carbamate (0.1 mole) in 650 ml water was fluorinated with elementary fluorine diluted with nitrogen (1:4) at 0-5°C until 4.5-5.0 liters of fluorine gas was passed into the reaction mixture. Oxidizing gases were evolved from the reaction mixture during the course of fluorination. At the end of the run the aqueous reaction mixture was extracted with five 50-ml portions of methylene chloride. The combined extracts were dried over Drierite and filtered, and the clear filtrate was concentrated. The residue, a colorless liquid, was fractionated, and after removal of 0.75 g of n-butanol, ca. 0.5 g of a colorless liquid, n_D^{25} 1.4130, was isolated and identified as n-butyl N-fluorocarbamate.

Calculated for $NHFCOOC_4H_9$:$C_5H_{10}FNO_2$:

C, 44.44; H, 7.46; F, 14.06; N, 10.37

Found: C, 44.90; H, 7.44; F, 18.40; N, 10.00.

e. Preparation of Ethyl N-Fluoro-N-Methylcarbamate

(1) Direct Fluorination of Ethyl N-Methylcarbamate

A solution of 26 g ethyl N-methylcarbamate (0.25 mole) in 350 ml H_2O was fluorinated with elementary fluorine diluted with nitrogen (1:4) at 0-5°C until ca. 11 liters of fluorine gas was passed into the reaction mixture. The reaction mixture was extracted with ten 75-ml portions of methylene chloride and the combined extracts were dried over Drierite. The filtered solution was concentrated and the residue distilled to give 16 g of pale yellow liquid, bp 70-73°C/100 mm, and 3 g of a colorless liquid, bp 83-85°C/0.1-0.3 mm.

The material of the first fraction was fractionated to give 3.0 g of yellow liquid, bp 60-74°C/100 mm, n_D^{25} 1.3941. The remaining product was found to be mainly ethyl methylcarbamate. The fraction n_D^{25} 1.3941 was redistilled and the middle cut, bp 50°C/10 mm, n_D^{25} 1.3869, was taken for infrared and elemental analyses. The infrared spectrum showed the absence of NH absorption at 2.8-3.4 μ, strong carbonyl, and several absorption bands in the NF region (10-12 μ).

Calculated for $C_4H_8FNO_2$ (m.w. 121.11):

C, 39.67; H, 6.66; N, 11.57; F, 15.69

Found: C, 39.10; H, 6.62; N, 11.97; F, 15.20.

(2) Methylation of the Sodium Salt of Ethyl N-Fluorocarbamate

The reaction was carried out in a 50-ml three-necked round-bottomed flask equipped with a stirrer, thermometer, and dropping funnel. A solution of 3.4 g sodium hydroxide (0.085 mole) in 20 ml water was placed in the flask. The solution was cooled to 0-5°C by means of an ice-water bath. To this alkaline solution was added dropwise from the dropping funnel, with stirring and cooling, 8.6 g ethyl N-fluorocarbamate (0.08 mole) over a period of 10 minutes. To the resulting solution of the sodium salt of ethyl

N-fluorocarbamate 5.05 g dimethylsulfate (0.04 mole) was added dropwise. The reaction was slow but exothermic, and the temperature of the mixture was kept at 5-10°C for a period of 60-70 min. A white solid (sodium sulfate) and pale-yellow oil separated during the course of the reaction. The reaction mixture was extracted with three 25-ml portions of methylene chloride and the combined extracts were dried over Drierite. The filtered solution was concentrated and the residue was distilled to give 4.5 g of pale yellow liquid, bp 20-22°C/0.5-1.0 mm, n_D^{25} 1.3900. The infrared spectrum of this material was identical to that of ethyl N-fluoro-N-methylcarbamate.

f. Preparation of Ethyl N-Chloro-N-Fluorocarbamate

This reaction was carried out in a 100-ml three-necked round-bottomed flask equipped with a stirrer and gas inlet and outlet tubes. The sodium salt of ethyl N-fluorocarbamate was prepared by dissolving 4.3 g ethyl N-fluorocarbamate (0.04 mole) in a solution of 1.6 g sodium hydroxide (0.04 mole) in 25 ml water at 0-5°C. The solution, together with 25 ml methylene chloride, was placed into the reaction flask. Chlorine gas* was passed into the cold (0-5°C), vigorously stirred mixture over a period of 45-60 min. At the end of the run the reaction mixture was allowed to warm to room temperature, the phases were separated, and the aqueous solution was extracted with two 25-ml portions of methylene chloride. The methylene chloride solution and the extracts were combined, dried over Drierite, and filtered. The filtrate was concentrated and the pale-yellow liquid residue was distilled to give 3.2 g of a colorless liquid, bp 30-40°C/20 mm, and 1.1 g of a pale-yellow liquid, bp 50-60°C/0.2-0.3 mm. The lower-boiling product apparently containing some residual solvent was fractionated. After removal of a forerun, a water-clear colorless liquid was obtained, bp 45°C/60-70 mm, n_D^{25} 1.4015. The infrared spectrum of this material showed absence of an NH absorption peak, strong carbonyl, and several absorption peaks in the NF region (10-12 μ).

*Commercial chlorine was condensed at -80°C until 1.82 ml of liquid was collected. This amount of liquid chlorine corresponds to 0.04 mole of the material. The liquid chlorine was allowed to evaporate and was passed into the reaction mixture by means of the gas inlet tube.

Calculated for $C_3H_5ClFNO_2$ (m.w. 141.54)

C, 25.46; H, 3.56; N, 9.90; F, 13.42

Found: C, 26.80; H, 3.50; N, 9.76; F, 11.60.

g. Preparation of Ethyl N-Bromo-N-Fluorocarbamate

To a mixture of 0.04 mole of sodium salt of ethyl N-fluorocarbamate in 15 ml water and 50 ml tetrachloride was added dropwise, with vigorous stirring at 0-5°C, elementary bromine until the bromine color was no longer observed. The reaction was completed in 10 min. The phases were separated and the aqueous phase was extracted with three 30-ml portions of carbon tetrachloride. The carbon tetrachloride solution and extracts were combined, dried, and filtered. The orange-yellow clear filtrate was concentrated to remove the solvent and the orange-red liquid residue was distilled to give 6.0 g of orange-yellow liquid, bp 30°C/0.1-0.3 mm, n_D^{25} 1.4425. The material was redistilled and the middle cut, bp 30°C/0.1-0.3 mm, n_D^{25} 1.4421, was taken for infrared and elemental analyses. The infrared spectrum of the product was found to be almost identical with that of ethyl N-chloro-N-fluorocarbamate.

Calculated for $C_3H_5BrFNO_2$ (m.w. 185.99)

C, 19.36; H, 2.71; N, 7.53; Br, 42.96; F, 10.20

Found: C, 20.00; H, 2.43; N, 7.60; Br, 45.00; F, 10.70.

h. Preparation of N-Fluoroiminodicarboxylate

(1) From Sodium Ethyl N-Fluorocarbamate and Chloroethylformate

The sodium salt of ethyl N-fluorocarbamate was prepared by dissolving, at 0-5°C, 5.4 g ethyl N-fluorocarbamate (0.05 mole) in a solution of 2.0 g sodium hydroxide (0.05 mole) in 50 ml H_2O. The solution was placed in a 100-ml round-bottomed three-necked flask equipped with a dropping funnel, thermometer, and stirrer. To the vigorously stirred solution

was added from the dropping funnel, at 5-10°C, 5.4 g ethyl chloroformate (0.05 mole) over a period of 10 min. The reaction was mildly exothermic and a pale-yellow oil separated gradually as the reaction progressed. After the addition of the ethyl chloroformate, the mixture was stirred for an additional 10 min. The mixture was extracted with two 25-ml portions of methylene chloride. The combined extracts were dried over Drierite and filtered, and the clear filtrate was concentrated to remove the solvent. The residue, a pale-yellow liquid, 8.5 g, was fractionated to give 6.5 g of yellow liquid, bp 53-58°C/0.1-0.3 mm, n_D^{25} 1.4140, and 1.0 g of a colorless liquid, bp 80-85°C/0.1-0.3 mm, n_D^{25} 1.4250. The lower-boiling liquid was redistilled and middle cut, bp 55°C/0.1-0.3 mm, n_D^{25} 1.4145, (3.0 g) was submitted for infrared and elemental analyses.

Calculated for $NF(COOC_2H_5)_2$:$C_6H_{10}FNO_4$:

C, 40.22; H, 5.63; F, 10.61; N, 7.82

Found: C, 40.25; H, 5.75; F, 10.90; N, 7.72.

(2) From Sodium Ethyl N-Fluorocarbamate and Ethyl N-Bromo-N-fluorocarbamate

The sodium salt of ethyl N-fluorocarbamate was prepared by dissolving 1.0 g ethyl N-fluorocarbamate (0.0093 mole) in 15 ml water containing 0.24 g sodium hydroxide (0.006 mole).* From a dropping funnel, 0.9 g ethyl N-bromo-N-fluorocarbamate (0.0048 mole) at 0-5°C was added, with stirring over a period of 5-10 min. The reaction mixture was stirred for 10 min, and at the end of the run the yellow oil was extracted with two 10-ml portions of methylene chloride. The combined extracts were dried over Drierite and filtered, and the clear filtrate was concentrated to remove the solvent. The yellow liquid residue was distilled to give 1.0 g yellow liquid, bp 35-45°C/0.1-0.3 mm, n_D^{25} 1.4165. The material was redistilled and a middle cut, bp 45-47°C/0.1 mm, n_D^{25} 1.4138, was collected. The infrared spectrum of the material was found to be identical to that of N-fluoroimino-dicarboxylate.

*An error was made in the calculations and an excess of N-fluorocarbamate was used in the preparation of the salt.

(3) From Sodium N-Fluorocarbamate and Dichlorofluoramine

The sodium salt of ethyl N-fluorocarbamate was prepared by dissolving 4.0 g ethyl N-fluorocarbamate (0.0374 mole) at 0-5°C in 30 ml water containing 1.5 g sodium hydroxide (0.0374 mole). The solution was placed in a 50-ml round-bottomed three-necked flask equipped with a stirrer and gas inlet and outlet tubes. Into the vigorously stirred solution (0-5°C) was passed via gas-inlet tube approximately 2 g of dichlorofluoramine over a period of 30 min. The reactor was connected in series with an evacuated infrared gas cell and a -80°C trap. The gaseous materials escaping from the reactor were found (infrared spectrum) to be a mixture of carbon dioxide, nitrous oxide, and dichlorofluoramine. Approximately 0.5 ml of the mixture, containing mainly unreacted dichlorofluoramine, was found in the -80°C trap at the end of the run.

At the end of the run the reaction mixture contained 1 to 2 ml of a heavy yellow oil which was extracted with three 10-ml portions of methylene chloride. The combined extracts were dried over Drierite, filtered, and concentrated. The residue, yellow oil, was fractionated to give 0.8 g of yellow liquid, bp 50-52°C/0.2 mm, n_D^{25} 1.4140. The infrared spectrum of this material was found to be identical in all respects with that of N-fluoroimino-dicarboxylate.

(4) Side Product in Chlorination of Sodium N-Fluorocarbamate

The side product obtained in chlorination of the sodium salt of ethyl N-fluorocarbamate, bp 50-60°C/0.2-0.3 mm, was subsequently identified as N-fluoriminodicarboxylate by comparing its infrared spectrum with that of an authentic sample.

i. Nitration of Ethyl N-Fluorocarbamate

To a solution of 2.7 g ethyl N-fluorocarbamate (0.025 mole) in 15 ml concentrated sulfuric acid at 0-5°C was added, with vigorous stirring, from a dropping funnel, 2.3 g ethyl nitrate (0.025 mole), over a period of 30 min. The reactor was connected in series with an evacuated infrared

gas cell. The reaction was very vigorous and large amounts of gaseous products were evolved. Infrared spectrum showed that the gaseous products were a mixture of carbon dioxide and nitrous oxide. No nonvolatile products of any kind could be isolated from the reaction mixture.

j. Decomposition of Aqueous Sodium Ethyl N-Fluorocarbamate

Into a 50-ml three-necked round-bottomed flask equipped with a dropping funnel, a stirrer, and a gas-outlet tube was placed a solution of 1.0 g sodium hydroxide (0.025 mole) in 20 ml of water. The reactor was connected in series with an evacuated infrared gas cell and a -80°C trap. To the cold (0-5°C), vigorously stirred solution was added from the dropping funnel 2.7 g ethyl N-fluorocarbamate (0.025 mole) over a period of 2 to 3 min. The reaction mixture was allowed to warm up to 20-25°C, at which temperature a slow gas evolution began. The decomposition was slow at this temperature, and after 25-30 min the mixture was heated up to 45-50°C and kept at this temperature for an additional 60 min, at which time the reaction was completed. The gaseous products escaping from the reaction mixture during the course of decomposition were found (by infrared spectrum) to be a mixture of carbon dioxide and some ethylene.

At the end of the run the reaction mixture contained some yellow water-insoluble oil and some white solid. The solid was removed by filtration and washed with methylene chloride. The solid was subsequently washed with cold water and with acetone. This solid was identified as sodium fluoride by comparing its infrared spectrum (KBr pellet) with that of an authentic sample.

The aqueous filtrate was extracted with five 20-ml portions of methylene chloride. The extracts were combined with methylene chloride washings, dried over Drierite, filtered, and concentrated. The yellow liquid residue was distilled to give 1.0 g of a colorless liquid, bp 95-105°C/0.1-0.3 mm, n_D^{25} 1.4320. The infrared spectrum of this material indicates that the compound is a carbamate. Partial elemental analysis showed the presence of 10.4% nitrogen.

k. Attempted Preparation of 1-Fluoronaphthalene

To a suspension of 3.85 g naphthalene (0.03 mole) in 15 ml concentrated sulfuric acid was added, at 0-5°C, 3.2 g ethyl N-fluorocarbamate (0.03 mole) from a dropping funnel. The reaction mixture turned somewhat dark in color, but no reaction was observed at this temperature. The mixture was heated up to 45°C, at which temperature the solid naphthalene disappeared in ca. 60 min and solid-deposited on cooling. The mixture was poured on ice and diluted to 200 ml with water. A clear solution resulted, indicating that the expected 1-fluoronaphthalene was not present. The aqueous solution possessed strong oxidizing properties, suggesting that unreacted ethyl N-fluorocarbamate was present. The solution was extracted with five 25-ml portions of methylene chloride and on working up the solution, ethyl N-fluorocarbamate was isolated and identified.

l. Attempted Preparation of N,N-Difluoroacetamide

A mixture of 0.6 g acetamide (0.01 mole) and 2.7 g ethyl N-fluorocarbamate (0.025 mole) was heated to 85-95°C and kept at this temperature for a period of 3 hr. Small amounts of gaseous products were evolved during the course of the reaction and the gaseous products were identified by infrared spectrum, as a mixture of carbon dioxide, nitrous oxide, and some ethylene. At the end of the run, most of the ethyl N-fluorocarbamate was recovered. Small amounts of unidentified yellow oil were also present in the reaction mixture. No trace of the expected N,N-difluoroacetamide could be detected in the reaction products.

m. Preparation of Dichlorofluoramine from N-Fluoroiminodicarboxylate

To 20 ml sodium hypochlorite (Clorox - 5.3% aqueous sodium hypochlorite) at 0-5°C was added with vigorous stirring 0.9 g N-fluoroiminodicarboxylate. The reactor was connected in series with a -80°C trap. After 15 min the reaction mixture was warmed to 15-20°C and kept at this temperature for a period of 30 min, at which time the gas evolution was completed. At the

end of the run 0.2-0.3 ml of a low-boiling pale-yellow liquid was present in the -80°C trap. A sample of the material was submitted for infrared analysis in a gas cell. The infrared spectrum of the material was identical with that of dichlorofluoramine (absorption peaks at 12 and 12.2 μ). The material was contaminated with carbon dioxide and nitrous oxide.

n. Attempted Fluorination of Naphthalene with N-Fluoroiminodicarboxylate

A mixture of 1.28 g naphthalene (0.01 mole) and 1.8 g N-fluoroiminodicarboxylate (0.01 mole) was heated to 90-95°C and kept at this temperature for a period of 7 hr. No reaction occurred under these conditions, and on cooling to room temperature the unreacted naphthalene crystallized out from the reaction mixture.

o. Preparation of Dichlorofluoramine

(1) From Ethyl N-Fluorocarbamate

To 150 ml sodium hypochlorite, Clorox, in a 250-ml three-necked round-bottomed flask equipped with a stirrer, dropping funnel, and gas-outlet tube was added at 0.5°C over a period of 20-25 min, 5.4 g ethyl N-fluorocarbamate (0.05 mole). The reactor was connected with a -80°C trap to condense volatile materials escaping during the course of the reaction. At the end of the run 0.3 ml of yellow liquid was in the -80°C trap, and there were larger amounts of the heavy yellow liquid on the bottom of the reaction flask. When the reaction mixture was allowed to warm up to 25°C, the yellow product distilled into the -80°C trap and ca. 1.7-1.8 ml of the material accumulated. The crude product was purified by trap-to-trap distillation and 1.7 ml was collected in a -20°C trap. A sample of the material was submitted for infrared analysis. The spectrum showed two very strong absorption peaks at 12.0 and 12.2 μ. Carbon dioxide was also present in the sample.

(2) From Ethyl N-Chloro-N-fluorocarbamate

Using an apparatus similar to that described above, 0.7 g of ethyl N-chloro-N-fluorocarbamate was added dropwise over a period of

5 min to 20 ml sodium hypochlorite (Clorox) at 0-5°C. At the end of the run, 0.25 ml of yellow liquid accumulated in the -80°C trap. The infrared spectrum of this material was found to be identical in all respects with that of dichlorofluoramine prepared from ethyl N-fluorocarbamate.

p. Hydrolysis of n-Butyl N,N-Difluorocarbamate

To 10 ml water in a 25-ml three-necked round-bottomed flask equipped with a stirrer, a dropping funnel, and a gas-outlet tube connected to a -80°C trap 1.3 g n-butyl N,N-difluorocarbamate at 0-5°C was added dropwise. No reaction took place at this temperature. After a few minutes the mixture was warmed to 50-55°C and kept at this temperature for a period of 20 min. During the warmup, the reaction mixture evolved oxidizing, gaseous material which condensed in the -80°C trap in the form of a colorless liquid. Only ca. 0.1 ml of the liquid was collected. A sample of the liquid was allowed to evaporate into an evacuated infrared gas cell and an infrared spectrum of the gaseous material was recorded. The spectrum was found to be identical in all respects with that of difluoramine, except that the material was contaminated with carbon dioxide.

q. Preparation of Chlorodifluoramine from n-Butyl N,N-Difluorocarbamate

To 20 ml of 5.3% aqueous sodium hypochlorite (Clorox, pH 10-10.5), 0.3 g n-butyl N,N-difluorocarbamate was added, at 0-5°C, with vigorous stirring. The reactor was connected in series with an evacuated infrared gas cell to collect gaseous products escaping from the reactor. After 15 min the reaction mixture was warmed to 30-35°C and a sample of gaseous material escaping from the reactor was subjected to infrared analysis. The infrared spectrum of the product was found to be identical to that of chlorodifluoramine. No other absorption peaks except those reported for chlorodifluoramine were present in the infrared spectrum.

r. Attempted Preparation of N-Chloromethylfluoramine

Ethyl N-fluoro-N-methylcarbamate (1.2 g) was added, with vigorous stirring, to 30 ml 5.3% aqueous sodium hypochlorite at 0-5°C. The reactor was connected in series with an evacuated infrared gas cell and a -80°C trap. No reaction occurred at 0-5°C. After 15 min the reaction mixture was heated to 40-45°C and kept at this temperature for a period of 1.5 hr. Again, no reaction of any kind was observed. At the end of the run the mixture was cooled to 20-25°C and extracted with methylene chloride. On working up the solution, ethyl N-fluoro-N-methylcarbamate was isolated and identified by comparing its infrared spectrum with that of an authentic sample.

C. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

Direct fluorination of aqueous urea to N,N-difluorourea and hydrolysis of the latter to the difluoramine were discovered at Aerojet-General more than a year ago.* Since that time, this process has been found quite useful in preparing difluoramine. The increasing importance of N,N-difluorourea as an intermediate for the preparation of difluoramine emphasizes the need for more information concerning the details of the reaction.

The fluorination of urea is run routinely in 4-mole batches. In several cases, for reasons not yet completely understood, the otherwise clear and colorless aqueous solution became yellow and turbid during the course of fluorination and, at the end of the run, deposited small amounts of yellow solid. A similar reaction was also noticed when the incompletely fluorinated aqueous difluorourea solution was allowed to age.

In one experiment, the yellow solid was isolated by filtering the cloudy aqueous difluorourea solution at the end of the fluorination. This solid was identified as biurea by comparison with an authentic sample. From the aqueous solution from which this product was recrystallized, a second material was also found, which was identified as azodicarbodiamide.

*High-Energy Oxidizer Binders for Solid Propellants, Aerojet-General Report No. 0371-02-2, July 1960 (Confidential).

The formation of biurea during the fluorination of urea suggests that monofluorourea, intermediate in the fluorination, reacts with urea to yield the product:

$$NH_2CONHF + NH_2CONH_2 \longrightarrow (NHCONH_2)_2 + HF$$

It is not clear why this side reaction occurred in only a few of the runs, although the coupling might be catalyzed by sunlight.

The direct fluorination of aqueous phenyl- or o-tolylurea was described in the previous quarterly report.* It was found that in both cases the same volatile liquid is produced. This material was found to contain four major components, one of which is present in ca. 70% concentration.

This component was also formed when an aqueous solution of difluorourea, hydrofluoric acid, and benzoquinone was allowed to stand at room temperature. To check the possibility that difluoramine, the hydrolysis product of N,N-difluorourea, was involved, a mixture of benzoquinone and aqueous difluoramine was kept at 20-25°C for a period of four days. No volatile reaction products were obtained although this observation, based on one experiment, is not conclusive.

The structure of this compound is not yet known. The molecular weight by vapor density, extrapolated to zero pressure, was determined to be 130. The NMR spectrum** showed fluorine, but no hydrogen. The sample size, however, was too small to give a well-defined F^{19} spectrum.

Attempts have been made to decompose the compound with either concentrated sulfuric acid or concentrated aqueous sodium hydroxide. In both cases no reaction took place even after prolonged standing at 45-55°C. The starting material was recovered.

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*Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 18 (Confidential)

**Dr. D. W. Moore, Naval Ordnance Test Station, China Lake.

2. Experimental

a. Attempted Hydrolysis of the Unknown Reaction Product of o-Tolylurea Fluorination

(1) Acid Hydrolysis

Ten ml of concentrated sulfuric acid was placed in a 50-ml three-necked round-bottomed flask equipped with a stirrer, gas-outlet tube, and dry ice-acetone reflux condenser. The top of the condenser was connected in series with a -80°C trap. To the vigorously stirred sulfuric acid 0.6 ml of low-boiling liquid (bp 24°C) obtained in direct fluorination of aqueous o-tolylurea was introduced at 0-5°C. No reaction was observed at 0-5°C and the mixture was warmed gradually to 40-45°C and kept at this temperature for a period of 2 hr. No gaseous products were produced during the course of this reaction (no pressure buildup) and the -80°C trap remained empty. At the end of the run, the dry ice-acetone condenser was allowed to warm up and the volatile material was distilled and accumulated in the -80°C trap. The volatile liquid was identified as starting material by infrared spectrum and amounted to 0.5 ml.

(2) Alkaline Hydrolysis

Using the apparatus described above, 0.4 ml of the material was added to a solution of 4.5 g sodium hydroxide in 10 ml H_2O at 0-5°C. No reaction occurred at this temperature, and the mixture was allowed to warm to 55°C, and was kept at this temperature for a period of 1 hr. At the end of the run the starting material was recovered quantitatively and identified by infrared spectrum.

b. Reaction Between Benzoquinone and Difluorourea

To a suspension of 11 g recrystallized benzoquinone (0.1 mole) in 200 ml H_2O was added, with stirring, 300 ml aqueous difluorourea (0.3-0.4 mole difluorourea and approximately 0.6-0.8 mole hydrofluoric acid) at 0-5°C. The reactor was connected in series with a -80°C trap. No visible changes occurred when the reaction mixture was allowed to stand for a period of 30 min. At this time, the cooling was halted and the reaction mixture was

allowed to warm to 25-30°C. At this temperature, some gaseous materials began to escape and the reactor contents turned progressively darker in color. The reaction mixture was allowed to stand overnight at room temperature. During this time 0.2-0.3 ml of a volatile colorless liquid accumulated in the -80°C trap. A sample of the product was submitted for infrared analysis and the spectrum was found to be identical with that of the product obtained from direct fluorination of aqueous o-tolylurea.

D. REACTION OF DICHLOROFLUORAMINE WITH TETRAFLUOROHYDRAZINE (P. M. Iloff)

1. Discussion

The reaction of dichlorofluoramine with tetrafluorohydrazine was attempted, with the objective of preparing chlorotrifluorohydrazine, a potentially valuable intermediate. A reaction took place readily at 0°C, when dichlorofluoramine was treated with excess tetrafluorohydrazine. The dichlorofluoramine was consumed, and a new material with approximately the same boiling point was formed. However, this material decomposed completely after several hours at room temperature, with the formation of chlorine, N_2F_2, and products of attack on glass.

The boiling point, spectral properties, and decomposition products of this material are in line with those expected for chlorotrifluorohydrazine. However, the observed instability indicates considerable difficulty in synthetic application. Dichlorofluoramine was found to be relatively stable under the conditions in the above reaction.

2. Experimental

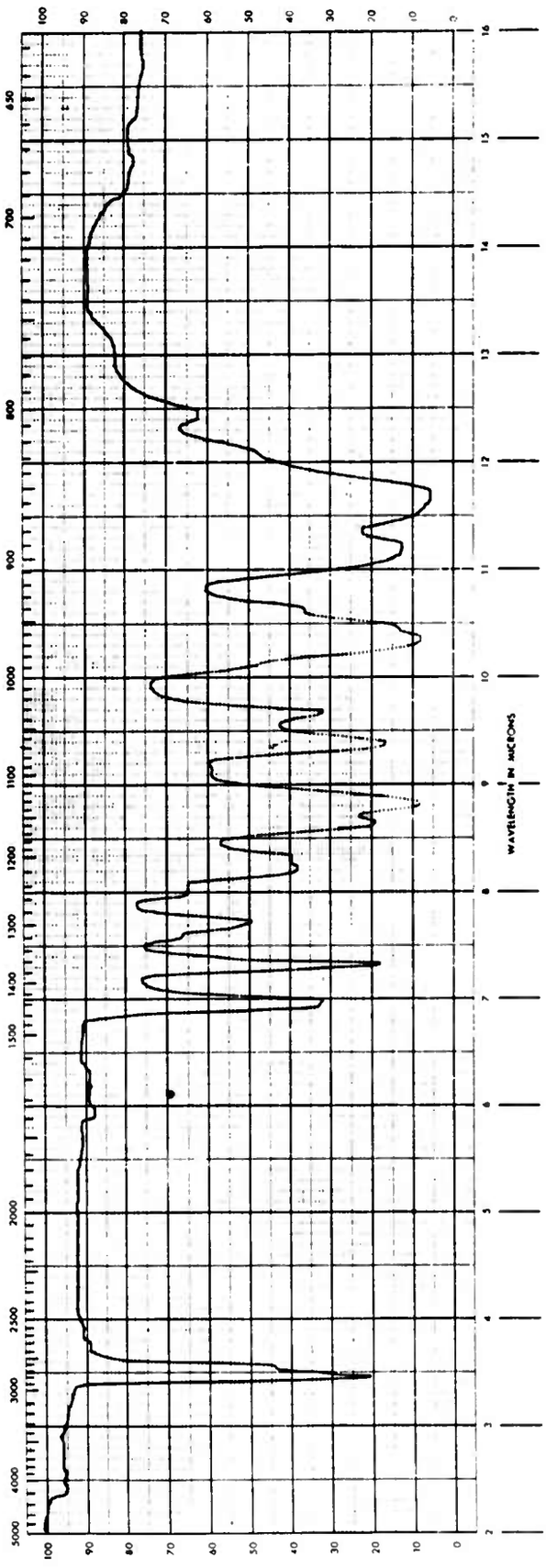
a. Reaction of Dichlorofluoramine with Tetrafluorohydrazine

A 1-liter Pyrex bulb was charged with N_2F_4 (16.5 mmoles) and Cl_2NF (2.97 mmoles) at -196°C. The bulb was then kept at 0°C for 5.75 hr. The gas was then passed slowly through a -80°C U-trap but nothing was stopped in the trap. The mixture was passed twice through a -126°C trap. The fraction that passed through, 16.5 mmoles, was shown to be mostly N_2F_4 with some $ClNF_2$ by

infrared absorption. The fraction held by the -126°C trap did not contain any Cl_2NF (infrared). It was passed through a -112°C trap twice and the material held at -112°C was removed immediately after each pass. The fraction held at -112°C was 1.23 mmoles of gas, consisting of NOCl and SiF_4 and negligible chlorine as indicated by infrared and ultraviolet absorption spectra. The fraction which passed through a -112°C trap (but was held at -126°C) consisted of 1.94 mmoles of gas. Infrared and ultraviolet spectra were taken at this time and after about three hours. The amount of chlorine (UV max. 335) increased, whereas infrared absorption bands initially present at 12.8 and 13.05 μ disappeared, and absorption bands between 10.3 and 11.0 μ decreased considerably. The infrared now showed definitely only the bands attributed to SiF_4, N_2O_4, and both the active and inactive forms of N_2F_2. The infrared cell used contained a glass stem which was attacked by the contents of the cell. There was no evidence of formation of a non-condensable.

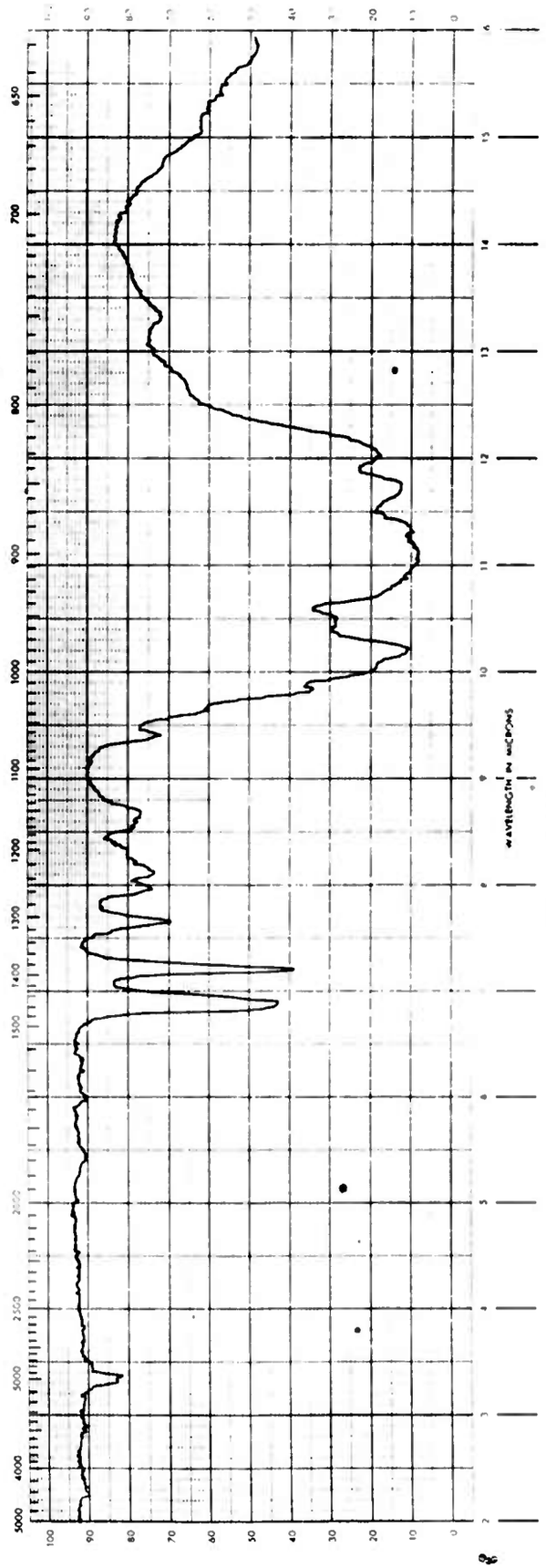
b. Stability of Cl_2NF

It was desired to find out if any decomposition of Cl_2NF would occur under the conditions of the above reaction. Thus, 3.06 mmoles of Cl_2NF was held in a Pyrex bulb at 0°C for 5 hr 35 min and then 2.67 mmoles of gas was recovered. This gas was shown to be nearly pure Cl_2NF with only traces of N_2O_4 and SiF_4, as shown by infrared absorption.



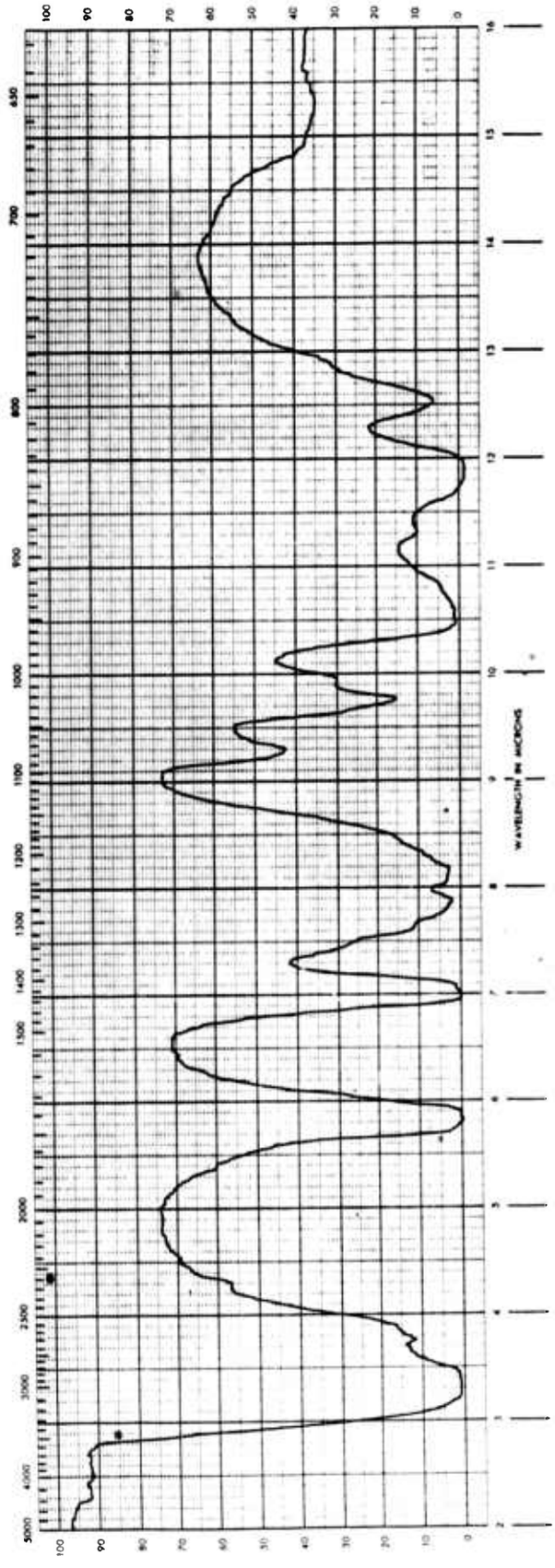
2,5-Dimethyl-2-(difluoramino)tetrahydrofuran

Figure 1



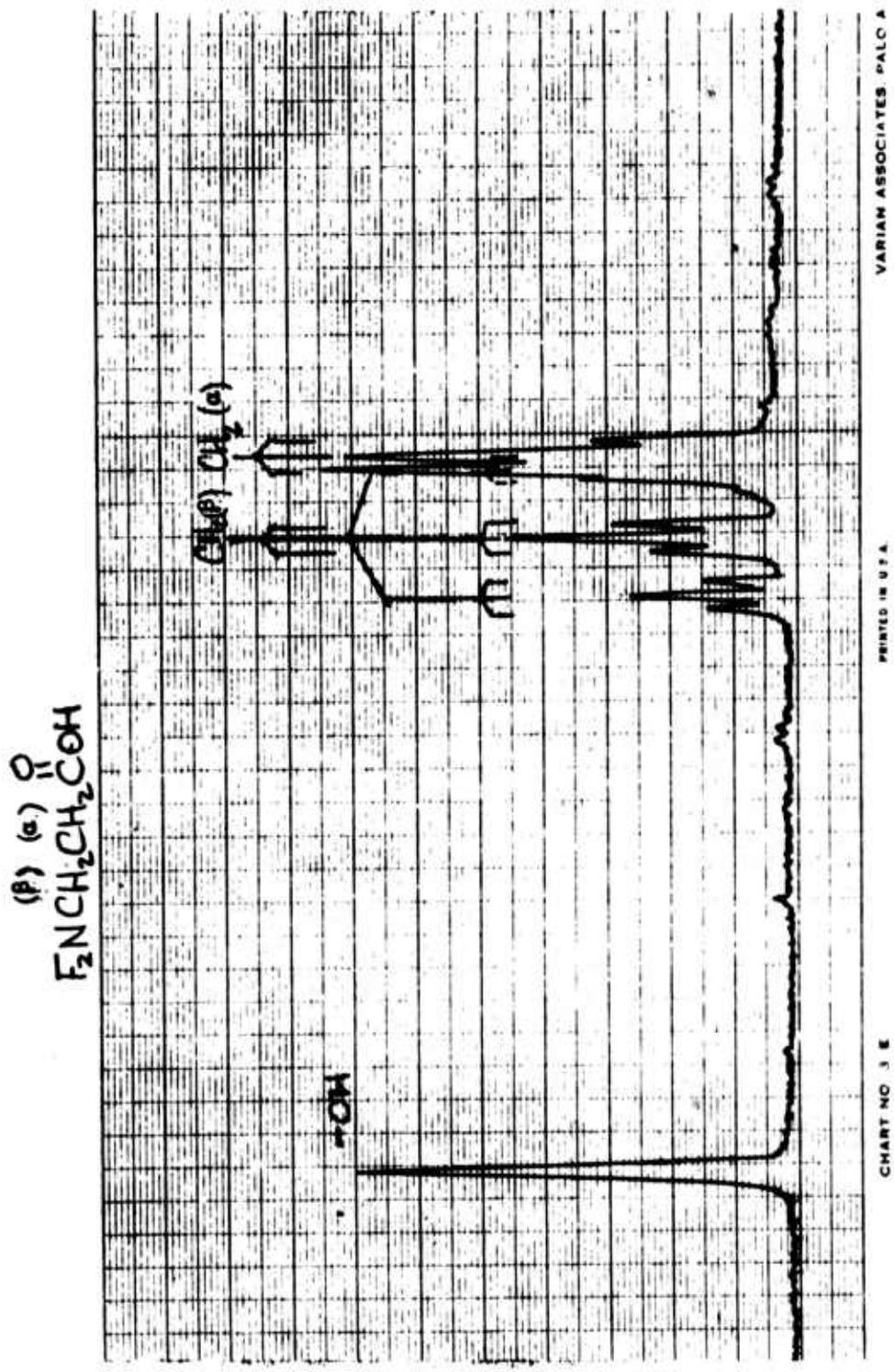
Tris(difluoramino)butane

Figure 2



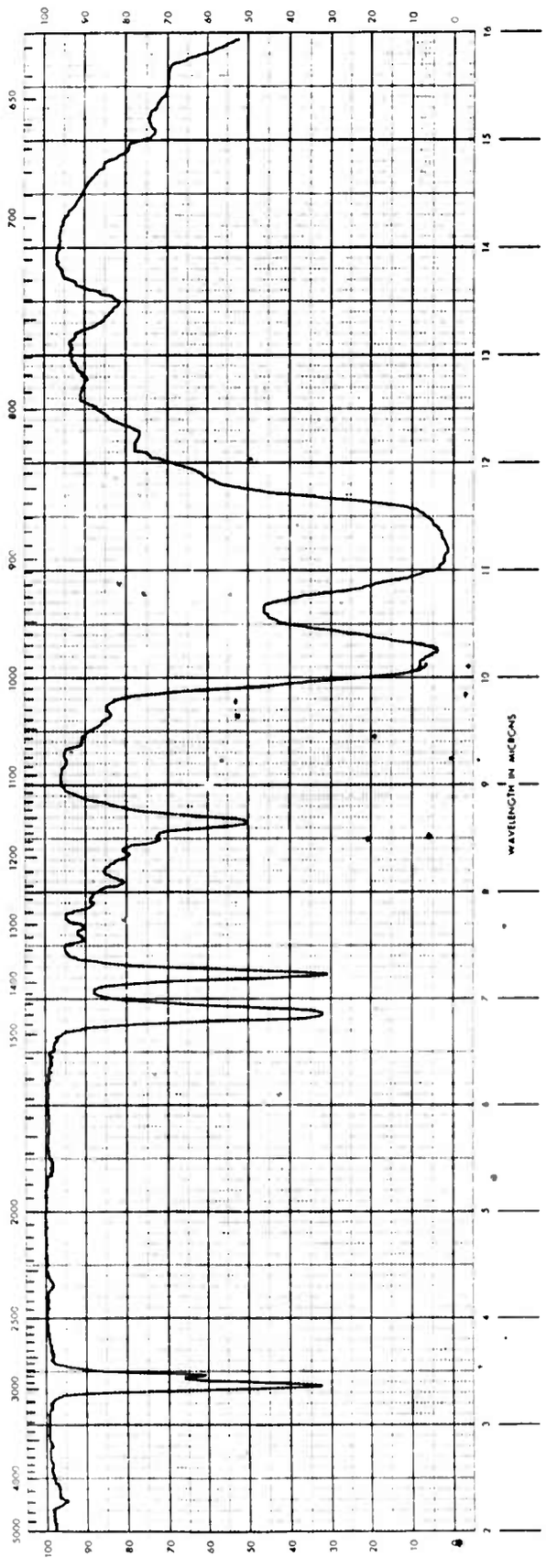
β-Difluoraminopropionic Acid

Figure 3



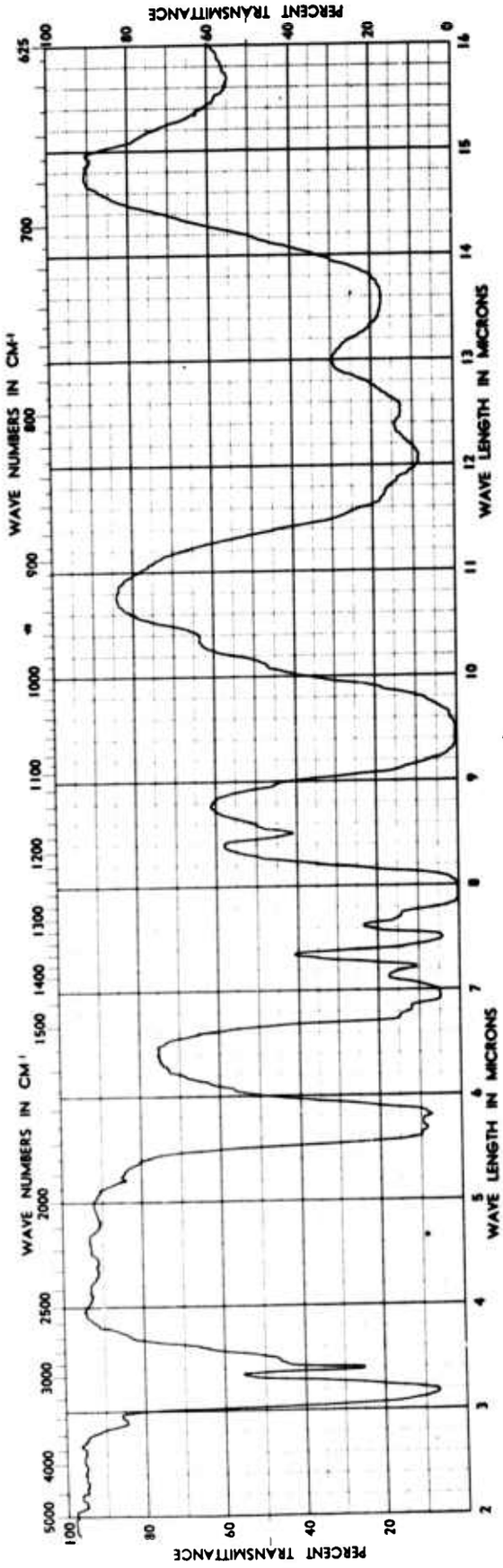
2,5,5-Trimethyl-2 - (defluoramino)tetrahydrofuran

Figure 4



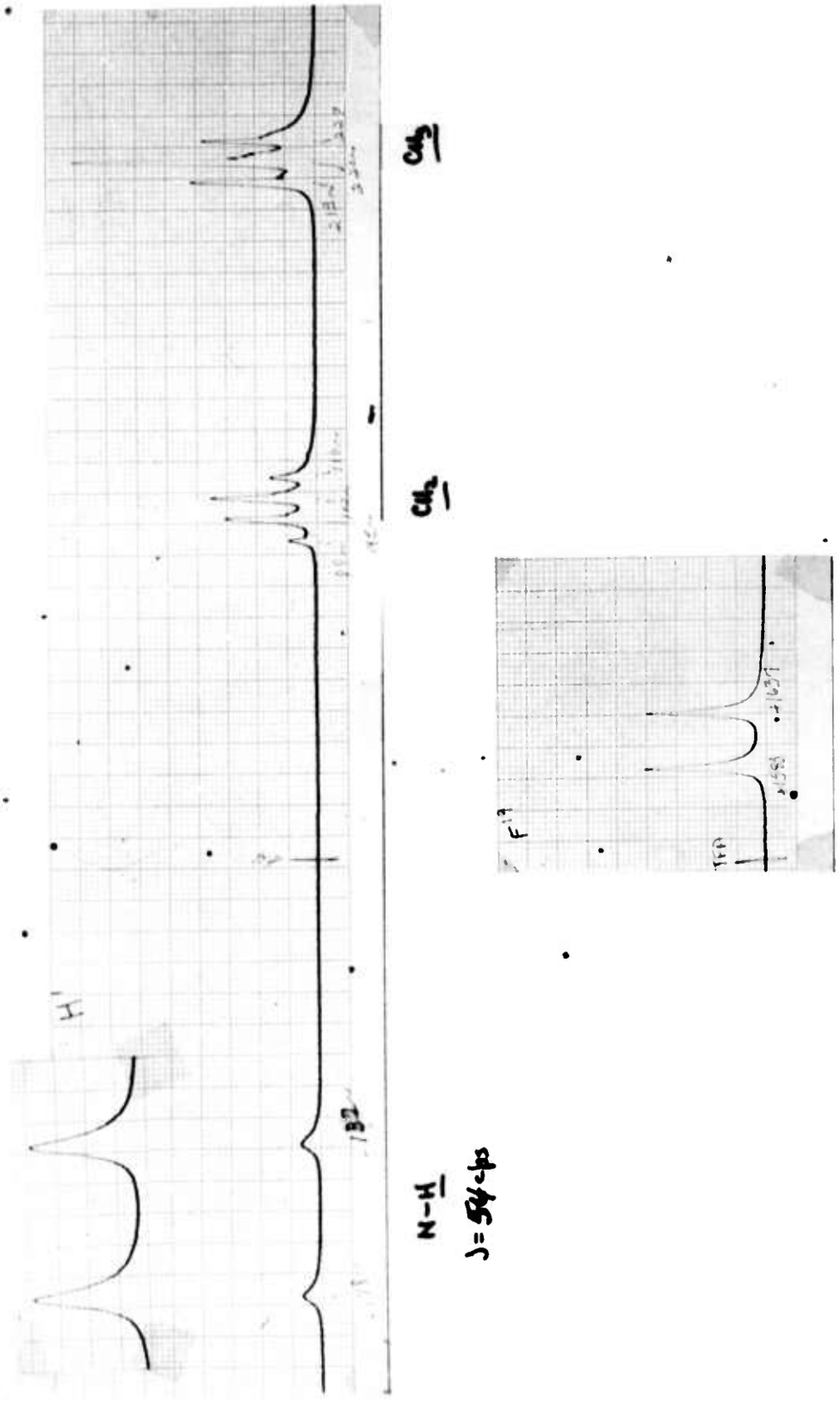
Product from 2,5-Dimethylfuran

Figure 5

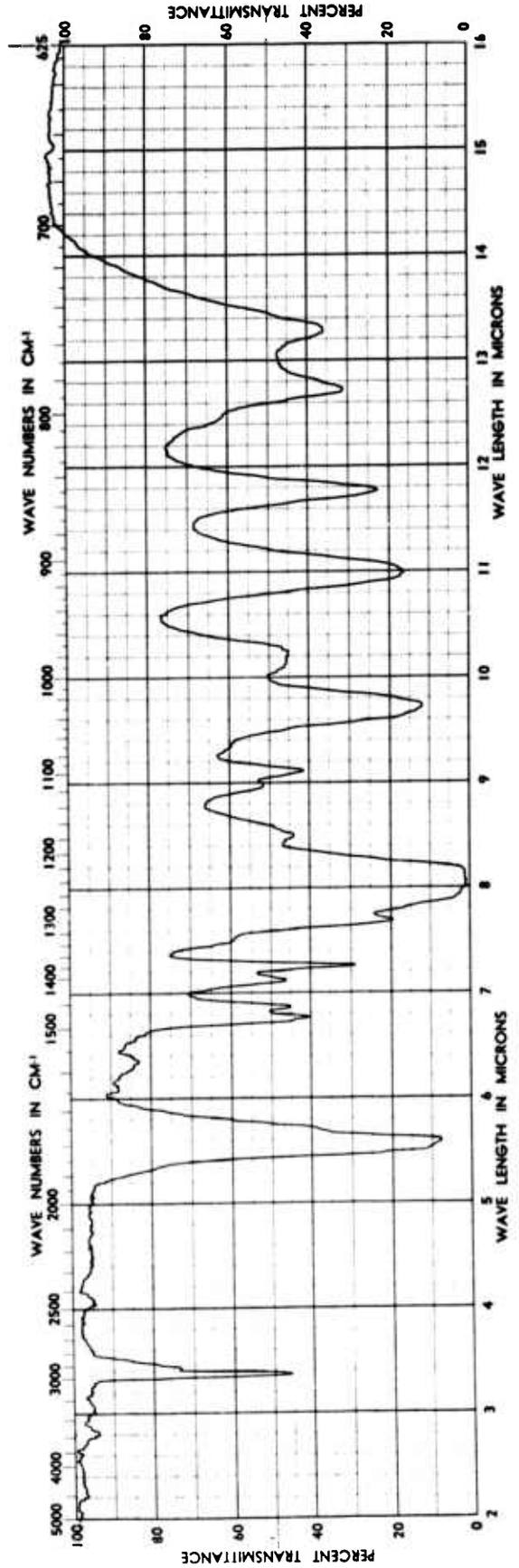


Ethyl N-Fluorocarbamate

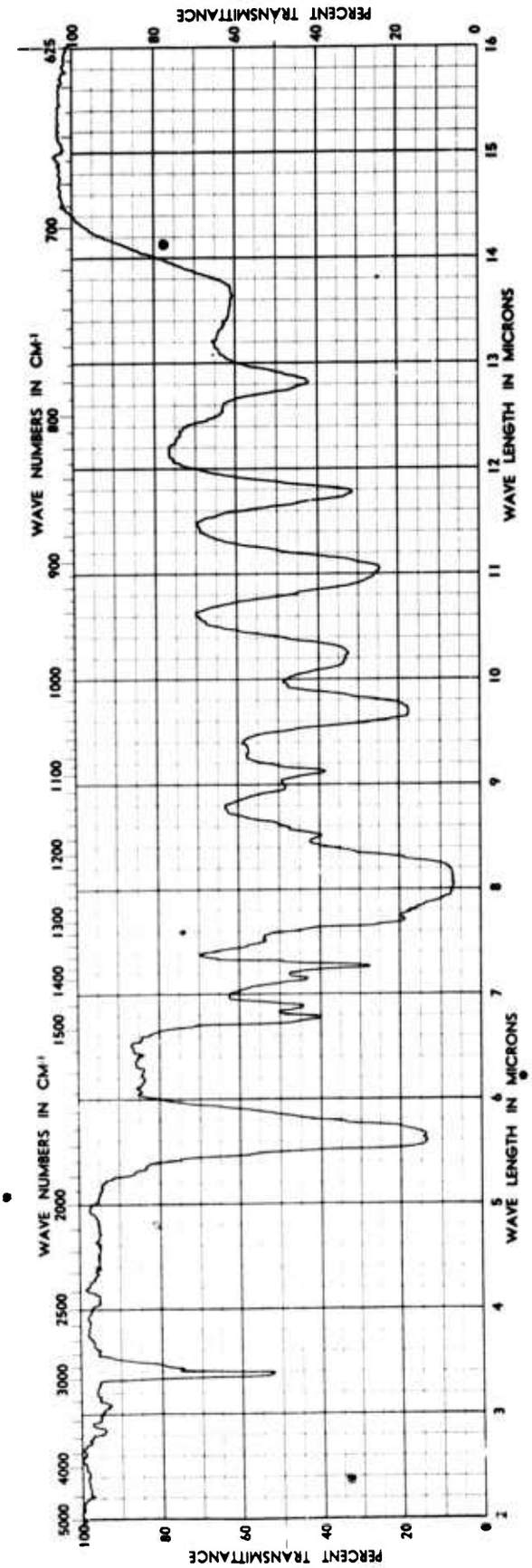
Figure 6



NMR Spectrum of Ethyl N-Fluorocarbamate

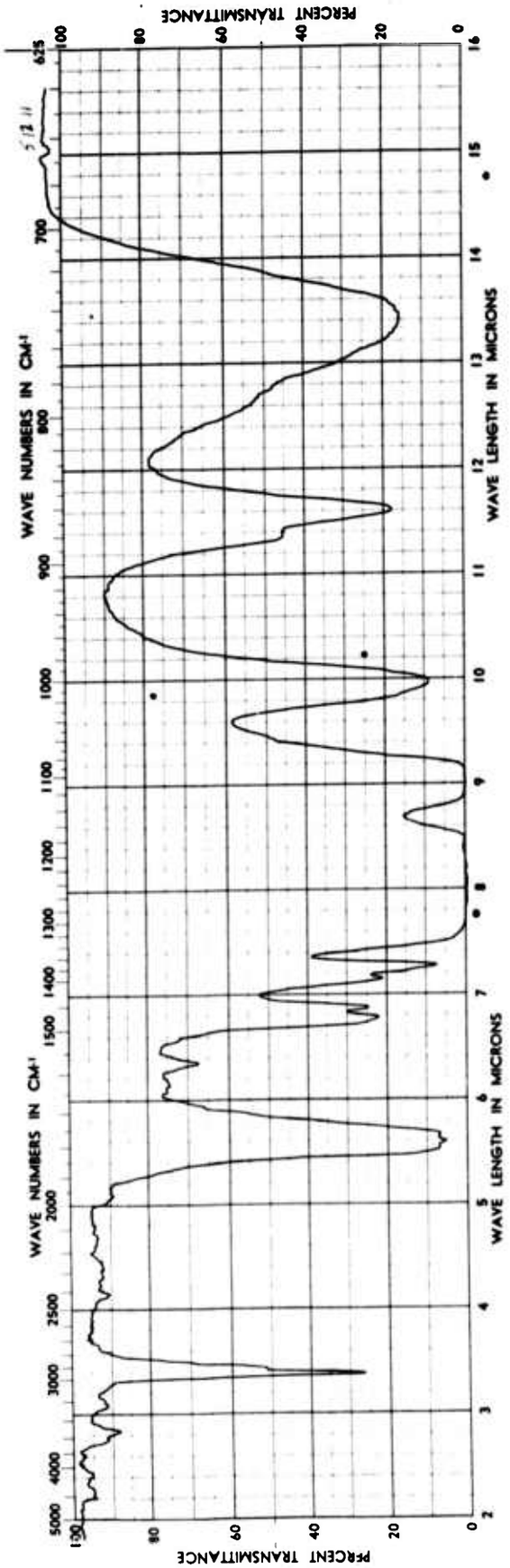


Ethyl N-Chloro-N-fluorocarbamate



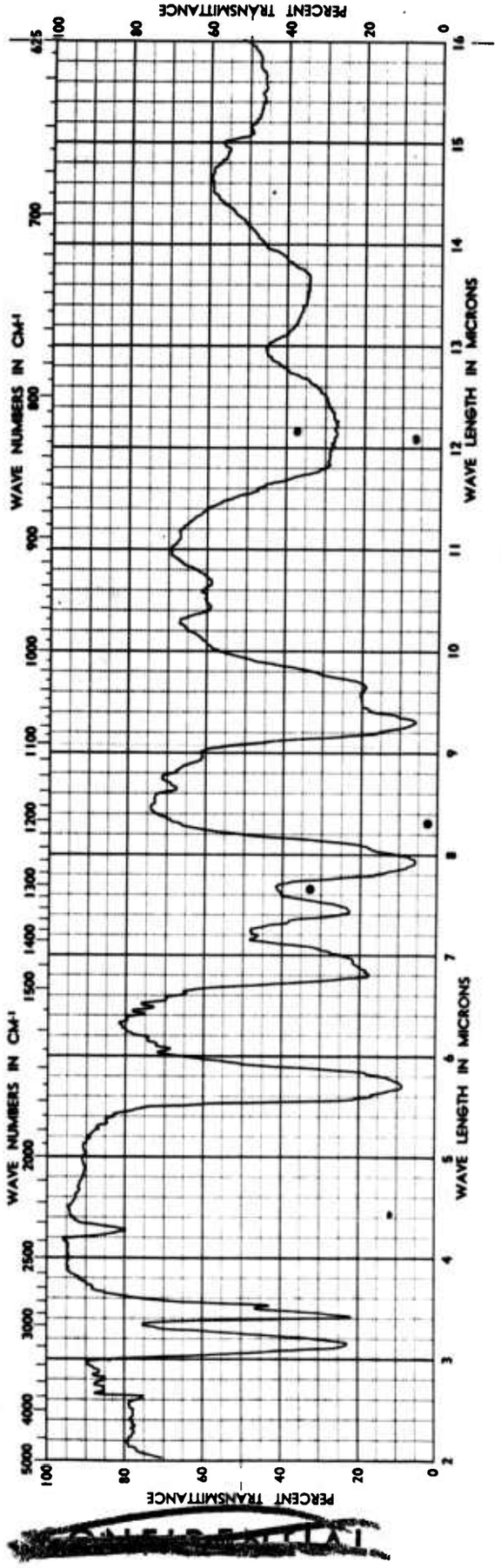
Ethyl N-Bromo-N-fluorocarbamate

Figure 8



N-Fluoriminodicarboxylic Acid Diethyl Ester

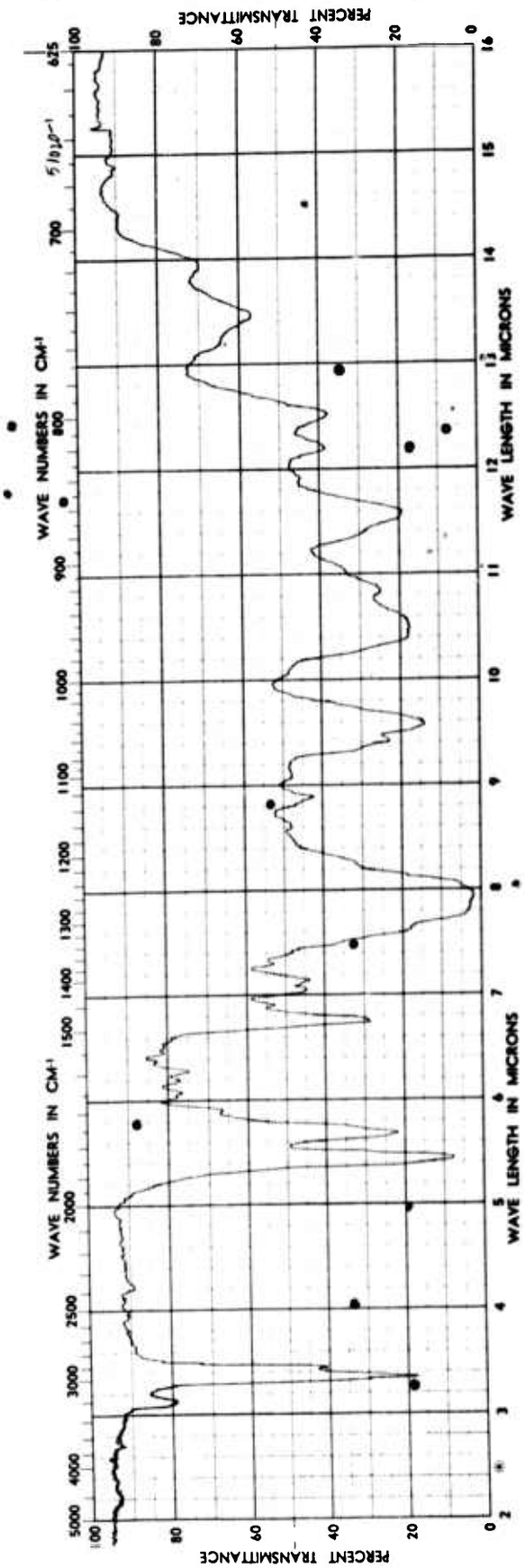
Figure 9



n-Butyl N,N-Difluorocarbamate

[redacted]

Figure 10



n-Buyl N-Fluorocarbamate

Figure 11

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